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Thin film cuprous oxide homojunction photoelectrode for water splitting

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Abstract

Employing cuprous oxide (Cu_2O) photoelectrodes in photoelectrochemical cells to generate hydrogen by water splitting is beneficial. Conventionally, it is limited in practice because of the well-known reasons of its inherent corrosiveness and poor conversion efficiencies. In this study, we have investigated the possibility of improving the efficiency of Cu_2O photoelectrode in the form of p-n homojunction together with sulphidation. Initially, the optimum pH values for the n- and p-Cu_2O thin film deposition baths are determined as 6.1 and 13 for Ti/n-Cu_2O/p-Cu_2O in photoelectrochemical cell configuration. Then, at these pH values the duration of n- and p-Cu_2O thin film deposition is optimized by forming Ti/n-Cu_2O/p-Cu_2O photoelectrode. In this study, we found that at 45 minutes of n-Cu_2O and 50 minutes of p-Cu_2O thin film deposition together with sulphidation forms relatively high efficient Ti/n-Cu_2O/p-Cu_2O photoelectrode resulting Solar-To-Hydrogen (STH) conversion efficiency of 0.9%. In addition, current-voltage characteristic of the best Cu_2O homojunction photoelectrode exhibits more negative shift in onset of photocurrent which indicates that photocurrent generation and transportation have improved by the formation of homojunction and further been enhanced by sulphidation.

Keywords

Cuprous oxide, Electrodeposition, Photoelectrode, p-n junction, Water splitting

Introduction

Generation of hydrogen energy by splitting water molecules in photoelectrochemical cell is a clean, environmentally friendly, renewable method of utilizing solar energy to address global energy crisis. Many efforts have been reported to date to harness hydrogen in PEC using different semiconductor materials as photoanodes, photocathodes or both (Nellist et al., 2016). Nevertheless, conversion of solar energy to hydrogen is not easy as reports show that electrochemistry involved in PEC configuration requires qualitative and efficient electrodes to make use of this sustainable energy source viable (Bae et al., 2017; Kafi et al., 2020; Siripala & Kumara, 1990).

Cuprous oxide (Cu_2O) is being investigated over years as one of the most reliable photoelectrode material as it is abundant, economical and pollution free. It is a well-known fact that Cu_2O photoelectrodes display low conversion efficiencies since they suffer from electrochemical corrosion, photocorrosion as well as unstable in PEC configurations. Many reports are available to aim at improving the quality of Cu_2O photoelectrodes (Liu et al., 2014; Siripala & Kumara, 1990; Wick & Tilley, 2015). Annealing, surface passivation, coupling of cuprous oxide to other materials have shown improvements in efficiency as well as stability of Cu_2O in PEC (Azevedo et al., 2014; Bornoz et al., 2014; Kafi et al., 2021).

In comparison to p-type Cu_2O photoelectrodes, studies on improving the stability and performance of n-type Cu_2O in PEC are rarely reported. Unlike p-type photoelectrodes,

in general n-type semiconductors exhibit aggressive photocorrosion in aqueous electrolytes as the thermodynamic oxidation potential lies above the O_2/OH^- redox potential (Wang & Gong, 2015). Further, the existence of high density of surface states together with slow kinetics for oxygen evolution reaction at electrode surface reduces the PEC performance. One possible solution is to modify the surface layer to reduce corrosion/photcorrosion and improve their chemical/photochemical stability when immersed in an electrolyte while allowing sufficient interfacial transfer of photogenerated minority carriers. Our previous reports have revealed that it is possible to improve the PEC water splitting capability of electrodeposited n-Cu_2O thin film electrodes as a result of sulphidation of n-Cu_2O thin film by eliminating electrically active high density of localized surface states (Kafi et al., 2020).

Another strategy to improve the efficiency of n-Cu_2O photoelectrodes in PEC water splitting system is that to combine it with p-Cu_2O thin film to form p-n junction photoelectrode (Wang et al., 2018). It can be expected that this p-n junction with built-in electric field effect between n-type and p-type Cu_2O will separate photogenerated carriers and enhances photocurrent density and photostability (Bai et al., 2019). Additionally, p-n junction photoelectrodes in PEC water splitting systems could increase electron-hole lifetime, efficient electron hole separation and the suppression of electron-hole recombination. Further, our previous studies imply that the sulphidation of Cu_2O thin film surfaces reduces surface reactivity in the sodium acetate aqueous electrolyte (Kafi et al., 2018a; Kafi et al., 2020; Kafi et al., 2021). Therefore, herein, we have investigated the possibility of improving the electrodeposited Cu_2O thin film electrode for watersplitting in PEC by forming p-n junction and modifying the Cu_2O p-n junction surface by sulphidation.

Methodology

n-Cu_2O thin films were potentiostatically electrodeposited on well-cleaned titanium (Ti) substrates at the film deposition bath pH value 6.1. Subsequently, thin films of p-Cu_2O were potentiostatically electrodeposited on these Ti/n-Cu_2O electrodes for bath pH values of 10, 11, 12 and 13. Durations of n- and p-Cu_2O thin film depositions were 60 and 45 minutes respectively (Kafi et al., 2018b). The growth conditions used for the n-Cu_2O and p-Cu_2O thin film deposition are available in our previous reports (Kafi et al., 2018a, 2018b). These Ti/n-Cu_2O/p-Cu_2O thin films were characterized in a PEC which consisted of 0.1 M sodium acetate (CH_3COONa) aqueous solution and determined the best pH combinations of n- and p-Cu_2O film deposition bath for Ti/n-Cu_2O/p-Cu_2O electrode preparation.

At the optimum pH combinations of n- and p-Cu_2O film deposition Ti/n-Cu_2O/p-Cu_2O electrode prepared by varying duration of n- and p-Cu_2O thin film deposition as listed in the Table 1 were characterized in the PEC. Then, these Ti/n-Cu_2O/p-Cu_2O thin film surfaces were exposed to 20 vol% ammonium sulphide (NH_4S) solution for 8 s and once again characterized in the above PEC to determine the effect of sulphidation. The counter and reference electrodes used in the PEC were a 2 cm × 2 cm platinum plate and a Ag/AgCl electrode respectively. Photoresponses and current-voltage (I-V) characterizations were done by using the Keithley multimeter and Gamry series G300 Potentiostat/Galvanostat/ZRA instrument respectively.

Table 1. *Durations of n- and p-Cu_2O thin film deposition of Ti/n-Cu_2O/p-Cu_2O electrodes at respective pH values of film deposition baths 6.1 and 13.0*

Combinations	Duration of thin film deposition (mins)	
	n-Cu_2O	p-Cu_2O
1	60	45
2	45	30
3	45	40
4	45	45
5	45	50
6	45	60

Results and Discussion

Figure 1 represents the photovoltage and photocurrent values obtained for Ti/n-Cu_2O/p-Cu_2O electrodes prepared by varying the pH values of the p-Cu_2O thin film deposition bath. According to Figure 1, it is clear that at the bath pH value 13 of p-Cu_2O thin film deposition both photovoltage and photocurrent values of Ti/n-Cu_2O/p-Cu_2O electrode are high and they are 161 mV and 128 μA cm^{-2} respectively. However, highest voltage is obtained for bath pH value 13 of p-Cu_2O thin film deposition.

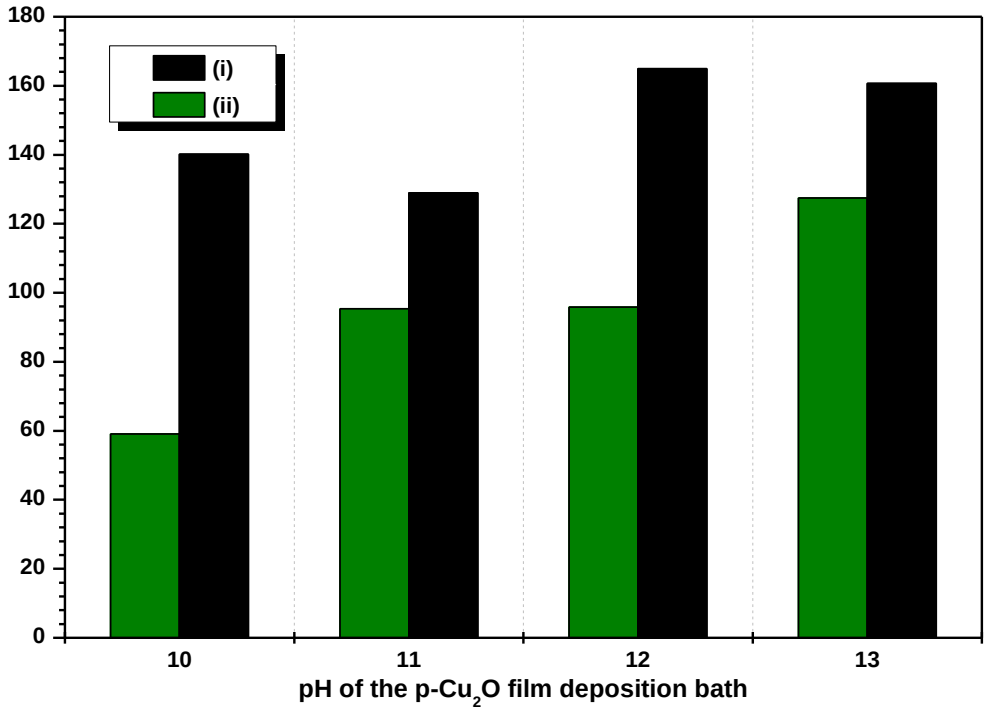

Figure 1. *Values of (i) photovoltage in mV and (ii) photocurrent density in μA cm^{-2} for Ti/n-Cu_2O/p-Cu_2O electrode in PEC at different pH values of p-Cu_2O thin film deposition.*

Additionally, it is noted that varying the durations of n- and p-Cu_2O thin films in preparation of Ti/n-Cu_2O/p-Cu_2O electrodes results in a considerable change in photocurrent value. Conventionally, the bare surfaces of Cu_2O in aqueous solutions could produce low photoresponses and thereby solar-to-hydrogen efficiencies (Kafi et al.,

2020). Our previous reports suggest that sulphidation of Cu_2O thin films using ammonium sulphide reduces the surface reactivity and improves the photoactivity of Cu_2O thin film surfaces (Kafi et al., 2018a; Kafi et al., 2020). Figure 2 represents the photocurrent values obtained for ammonium sulphide treated and untreated Ti/n-Cu_2O/p-Cu_2O electrodes prepared for selected n- and p-Cu_2O thin film deposition times listed in Table 1. It is very clear that sulphidation of Cu_2O thin film surfaces has significantly increased the photocurrent values of Ti/n-Cu_2O/p-Cu_2O electrodes in PEC configuration. The combination 5 listed in Table 1 has proven to be the best photoelectrode in PEC configuration and the I-V characteristics of this is presented in Figure 3.

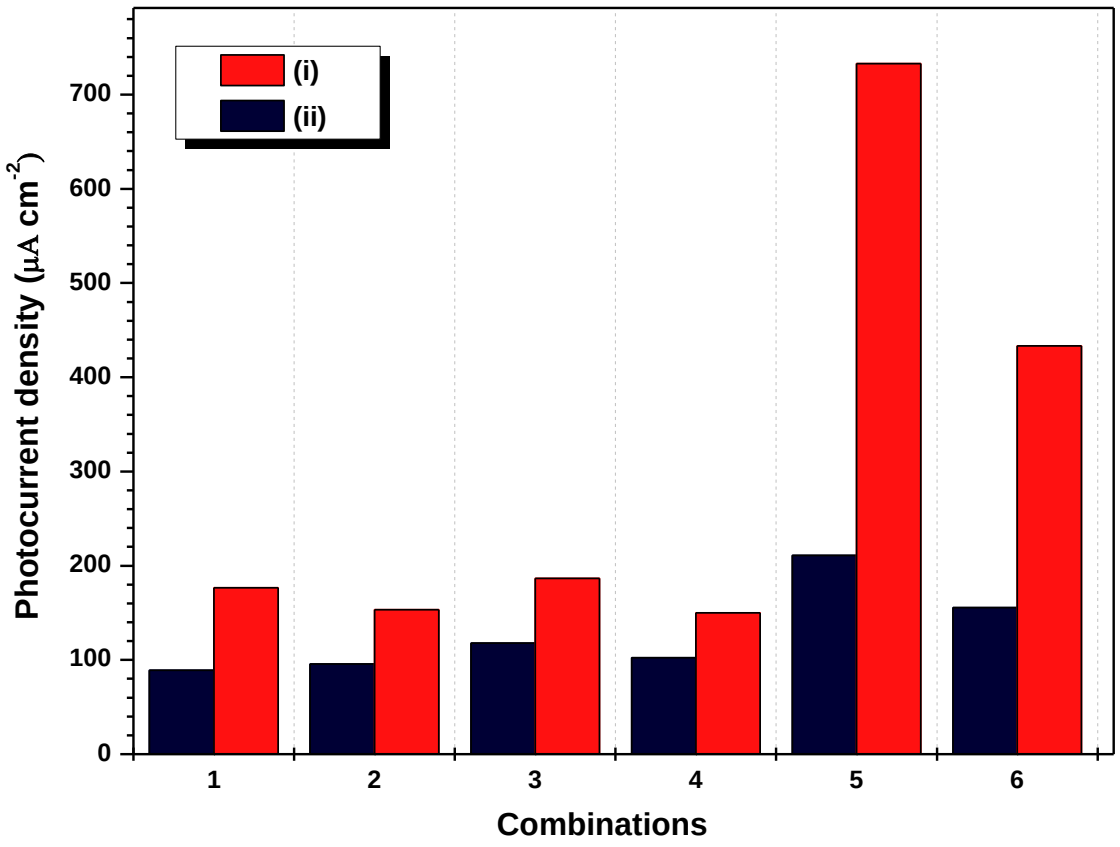

Figure 2. *The resulted photocurrent values of Ti/n-Cu_2O/p-Cu_2O electrodes (i) with and (ii) without treating with ammonium sulphide fabricated for different durations of n- and p-Cu_2O thin film deposition as listed in Table 1.*

In comparison to our previous work on n-Cu_2O in PEC (Kafi et al., 2020), it is evident that Cu_2O homojunction in the same PEC develops higher built-in-potential. This can be observed by comparing the on-set potential of I-V curves in Figure 3. However, the resulted Cu_2O homojunction in PEC produces relatively low STH conversion efficiency. Further parameterization of the Cu_2O homojunction, modification of photoelectrode configuration as well as PEC configuration could improve the production of hydrogen by splitting water molecules.

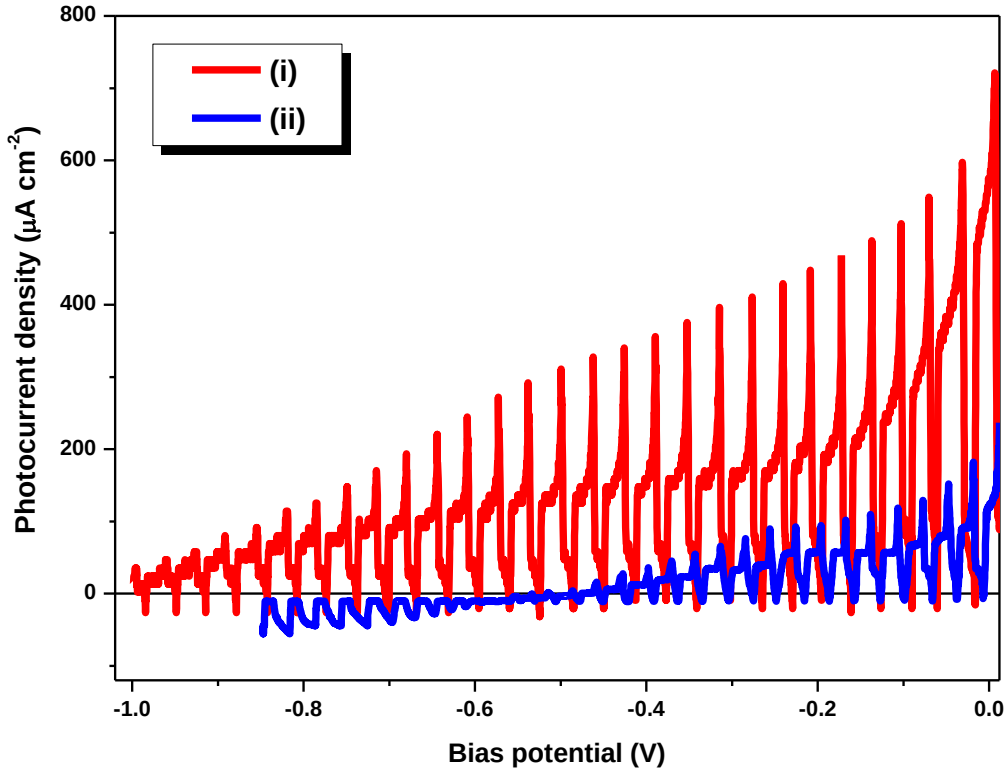

Figure 3. *I-V characteristics of Ti/n-Cu_2O/p-Cu_2O electrode (i) with and (ii) without treating with ammonium sulphide for the combination 5 considered in Table 1.*

Conclusion

In summary, the study revealed that the PEC water splitting by a Cu_2O homojunction depends on both pH and duration of n- and p-Cu_2O film deposition. Further, the conversion efficiency of STH has been enhanced by the sulphidation. The best Cu_2O homojunction photoelectrode has STH value of 0.9%. In addition, it is notable that the built-in potential is increased in formation of Cu_2O homojunction and after the sulphidation of Cu_2O homojunction. It can be concluded that further optimization of Cu_2O homojunction together with sulphidation could enhance the performance of Cu_2O homojunction photoelectrode in PEC water splitting.

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