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Properties Enhancement of Cu_2O/TiO_2 Heterostructure Film Using Two-step Hydrothermal and Potentiostatic Deposition Method

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ABSTRACT

Two-steps hydrothermal were demonstrated to create a high efficiently interfacial layer of TiO_2 thin film. The first hydrothermal was conducted to synthesize a well-aligned and compact structure of TiO_2 nanorods on FTO substrate. Etching treatment in an acidic medium of hydrochloric acid (HCl) as a second hydrothermal favors increasing the surface area prior to any deposition to be a heterostructure film. The morphology of nanorods changed while the electrical resistivity decreased, demonstrating that the etching treatment had a substantial effect on the TiO_2 thin film properties. Cyclic voltammetry (CV) was conducted prior deposition. The electrodeposition of Cu_2O on the TiO_2 thin film was fabricated by using copper acetate-based solution with pH value of 12.0 at bath temperature of 60°C. The finding revealed that the pyramidal structure of Cu_2O film was deposited uniformly, which is believed that the properties of TiO_2 interfacial layer were excellently improved.

Keywords: *Cyclic voltammetry, Etching treatment, Heterostructure, Hydrothermal, Potentiostatic deposition*

1. INTRODUCTION

The development of Cu_2O/TiO_2 heterostructure as a potential solar cell contender has been shown in several research. Nevertheless, the efficiency remains poor, and the best result is below the theoretical limits of 20% of Cu_2O [1] and 11% of TiO_2 in the application of dye-sensitized solar cells (DSSC) [2]. Hussain et al. claim that the band discontinuities, substantial lattice mismatch, p-n junction interface defects, fast electron and hole pair recombination rate are the main causes of the decreased efficiency of Cu_2O/TiO_2 heterostructure film [3,4]. Rapid recombination events occur near the p-n junction contact, where the carriers' traps are located. Due to the possibility of electron and hole energy loss in the trapped channel, which raises the recombination rate, such barriers reduce the efficiency of photogenerated carriers.

Li et al. discovered that a lower open circuit voltage is the cause of the poor efficiency of Cu_2O/TiO_2 radial p-n junctions. This is the result of the shunt resistance and reverse saturation current fluctuating originated from the junction interface defects [5]. Previous research on the Cu_2O/TiO_2 fabrication heterojunction films suggested that a significant factor influencing the efficiency of photovoltaic performance is the state of the p-n junction interfacial [3]. The obstacles at the junction need to be reduced to ascertain the carrier's mobility are seamless. This can be accomplished by increasing the conductive mechanism via the structure modification. Therefore, this research concerns on the modification of TiO_2 nanorods since this structure provides direct channels for electron transportation at the TiO_2/FTO and Cu_2O/TiO_2 interfaces.

The status of Cu_2O/TiO_2 heterojunction solar cells development is practising on the anatase phase of TiO_2 when depositing the Cu_2O layer. However, the anatase phase is meta-stable upon heat treatment compared to the rutile phase that exhibits sturdy and high stability towards chemicals and temperature changing [6]. The rutile phase and structure modification perhaps are the solution key to improve the interfacial layer of TiO_2 properties for promoting the Cu_2O deposition uniformly. It is known that the Cu_2O could deposit on various surfaces, however, the uniformity issue of Cu_2O growth associated with substrate resistance is not really highlighted. The low resistance of substrate is indispensable for Cu_2O growth uniformly and such low resistance of underlayer would be achieved by a surface modification of TiO_2 nanorods in a highly acidic medium to become an efficient interfacial layer. The efficient interfacial layer is beneficial for promoting the Cu_2O particles to be deposited uniformly thus improve the p-n junction properties in heterojunction solar cell development.

2. MATERIALS AND METHODS

In this work, three main phases of experimental procedures were conducted to fabricate the heterostructure thin film. The first phase is to synthesize a well-aligned of TiO_2 nanorods structure on the FTO substrate using the hydrothermal synthesis. Second hydrothermal process was conducted to the TiO_2 film in HCl medium where the process is called etching treatment. Prior to Cu_2O deposition, CV was demonstrated, followed by a conventional electrodeposition of Cu_2O film in copper-acetate based solution. The as-prepared sample was synthesized based on the conditions as shown in Table 1.

Table 1 Conditions of the main phases in Cu_2O/TiO_2 heterostructure film fabrication

Phase	Solution	Reaction time
TiO_2 synthesis	DI:HCl:TBOT	8 hours
TiO_2-HCl treated	DI:HCl	5 hours
Cu_2O deposition	DI:Cu(Ac)$_2$.H_2O:Lactic Acid	60 minutes

2.1. TiO_2 Nanorods Synthesis

The substrates used here are pieces of FTO glass (7 Ω/sq.) measuring 15 mm by 25 mm and having a thickness of 2.0 mm. These substrates underwent 10-minute ultrasonic cleaning treatments in acetone, ethanol, and deionized water. The mixture of deionized water and hydrochloric acid (36.5–38% by weight) was stirred for 5 minutes with a volume of 60 mL respectively. A calculated amount of titanium (IV) butoxide (TBOT) was added dropwise into the mixture and stirred for an additional 10 minutes. The FTO substrates were positioned with the active side facing down against the Teflon wall of an autoclave that had been lined with Teflon. After that, the autoclave was totally shut off, and hydrothermal synthesis was carried out for 8 hours at 150°C. The substrates were removed once they had cooled to room temperature, thoroughly cleaned using deionized water, and dried naturally [7]. The process is known as the first step of hydrothermal process.

2.2. TiO_2 Etching Treatment

The second hydrothermal was conducted on the as-sensitized TiO_2 nanorods film. A transparent etching solution was made by adding hydrochloric acid (36.5-38% by weight) to deionized water and vigorously stirring the mixture and placed in a Teflon-lined vessel with TiO_2 nanorods film facing upwards. Then, the Teflon-lined vessel was sealed completely in a stainless-steel autoclave and put inside the oven where the hydrothermal process was carried out at 150°C for 5 hours. The etched TiO_2 nanorods samples were removed once they had cooled to room temperature, washed for 2 hours in deionized water to eliminate any trace of acid, and then dried in the air [8].

2.3. Cu_2O Electrodeposition

The electrodeposition process was conducted to deposit the Cu_2O thin film onto the nanorods-TiO_2/FTO glass substrate. Conventional electrochemical cell consisting of three electrodes was utilized for fabrication. Through potentiostatic electrolysis, a solution comprising lactic acid and copper (II) acetate monohydrate was employed to deposit the Cu_2O film onto etched TiO_2 nanorods with target deposition area 1.0 cm^2. The potassium hydroxide (KOH) was added to modify the pH of the solution. After setting the pH solution to 12.0 and the temperature of 60°C, the electrodeposition was carried out for 60 minutes. The Cu_2O thin film was cathodically accomplished at potential of -0.4 V vs Ag/AgCl [9].

2.4. Characterization Techniques

The as-prepared films' crystal structure investigated using PANanalytical X-Pert^3 Powder X-ray diffraction spectroscopy (XRD) with CuK_α radiation (λ) 1.5406 Å wavelength in the Bragg angle range of 20° to 80° at a scanning speed of 2°min^{-1} with employment fixed divergence slit. The voltage and current of the X-ray tube were adjusted to 40 kV and 40 mA, respectively. The samples' morphology was carried out using field emission scanning electron microscopy (FE-SEM, JOEL, JSM-7600F). A 4Point Probe (Signatone Pro4-440N) was connected to the source meter to ascertain the resistivity properties of the samples.

3. RESULTS AND DISCUSSION

The as-prepared samples are discussing on the crystallinity, morphology, and the resistivity of the film. The characterization of the TiO_2 nanorod sample will not be discussed here, since the properties had been extensively discussed in previous studies [10,11].

3.1. Cyclic Voltammetry

Prior to the Cu_2O deposit, the CV measurement was performed in the cell configuration that is similar as the classical standard of electrodeposition in aqueous solution consisting of 0.4 M of copper acetate and 3 M lactic acid. The pH of the solution was adjusted to 12 and was achieved by the addition of KOH, while the bath temperature was set to 60 °C. Data voltammogram for Cu_2O yielded in the range of +0.5 and -1.0 V vs. Ag/AgCl with a 5 mV/s of scan rate conducted on the etched TiO_2 nanorods samples, as displayed in Figure 1. It was observed that the scanning was swept to the negative potential side attributed to the reduction reactions and this confirmed the presence of cupric ions Cu^{2+} in the electrolyte.

As shown in Figure 1, the voltammogram for as-prepared samples reveals the presence of two cathodic peaks, which is confirming the two reductions reactions for Cu^{2+} ions. The first peak, which has a region with red dashed lines around it, was attributed to the reduction of Cu^{2+} ions into Cu^+. After that, the Cu^+ ions migrate to the cathode for copper hydroxide, Cu (OH) formation. In the electrolyte solution, the produced Cu^+ ions interact with the OH^- ions to form the compound of Cu_2O. Copper metal (Cu^0) is formed with reduction of Cu^+ ions, and this is linked to the second reduction peak. The development of hydrogen could be observed, nevertheless, if the applied potential was less than −1.2 V. The presence of cathodic peak in the potential window with the range of -0.32 to -0.56 V. Beyond the potential of -0.56 V, the formation of Cu could occur due to the reduction of Cu^+ to Cu^0.

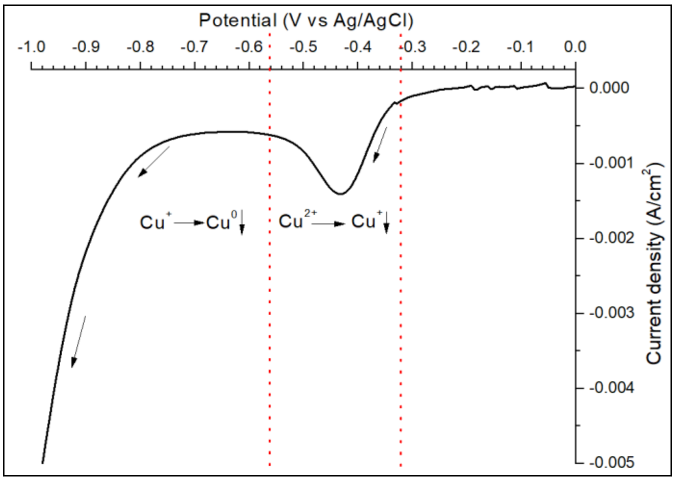

Figure 1. Voltammogram of Cu_2O on TiO_2 HCl-treated sample in 0.4M copper acetate, 3M lactic acid and KOH.

The CV was conducted with two main purposes. First is to identify the appropriate potential of electrodeposition of Cu_2O on TiO_2 structure and second is to avoid the disproportionate reaction of Cu_2O in low pH solution. The latter could be prevented by complexing with the lactate ions that stabilised the Cu^{2+} ions at high pH level. Moreover, lactate ions help in minimising the free cupric ions and inhibit the formation of $Cu(OH)_2$ precipitation that typically occurs in highly concentrated alkaline solutions [12]. In this work, the Cu_2O film was electrodeposited by applying the potential of – 0.4 V vs. Ag/AgCl because at this potential value, a smooth and dense structure of Cu_2O could be obtained [13]. The electrodeposition was performed at 60 minutes time deposition for TiO_2-HCl treated sample.

3.2. Structural Analysis

Figure 2 reveals the domination of cuprite peaks in the XRD diffraction pattern for as-prepared samples. These peaks were situated at 2θ values of 29.7°, 36.6°, 42.3°, 61.5°, 73.7°, and 77.7° and corresponded to (110), (111), (200), (220), (311), and (222) planes. It is also noticeable that the intensity of (111) Cu_2O exhibited as the strongest diffraction peak besides the presence of peaks indexed to SnO_2 and TiO_2 but in weak intensity. It was reported that the electrodeposition that was carried out in an alkaline solution of pH 12, the (111) plane exhibited as the strongest preferential facet [14] and suggests that the more desirable p-type Cu_2O has been synthesized [15], in line with this study.

It also evidently suggested that Cu_2O has grown and encompassed uniformly on the TiO_2 HCl-treated samples, due to the acceleration of Cu_2O deposition rate, which is believed improving with the HCl etching treatment. Such deposition rate improvement is possibly come from slender nanorod morphology and low resistivity of interfacial layer TiO_2 film when prolonged the etching time to 5 hours. This attributes to the acceleration of crystalline Cu_2O growth on TiO_2 HCl-treated that left behind the weak peaks. Moreover, it demonstrates that a larger exposed orientation of Cu_2O nanocrystalline when TiO_2 HCl-treated becomes the substrate layer.

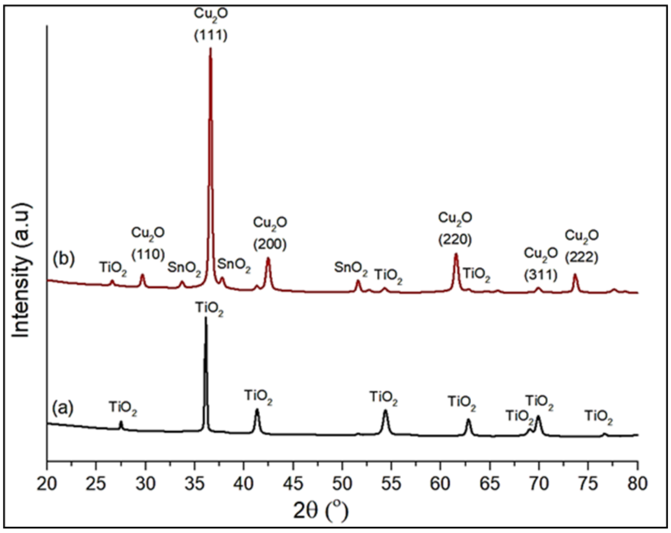

Figure 2. XRD patterns of TiO_2 HCl-treated (a) before and (b) after Cu_2O deposition.

The Scherrer equation is given by D = Kλ / β cos θ and used to determine the crystallite size of the cuprite (Cu_2O) phase. D is a crystal size; K is a constant and usually taken to be 0.9; λ is the wavelength of the X-ray radiation (λ = 0.15406nm) for CuKα; and β is the line width at half-maximum height (FWHM), while θ (theta) is half of the diffraction angle in radians. It can be suggested that by 5 hours etching duration of TiO_2 nanorods as substrate leads to a larger crystallite size, which relative to a narrow FWHM obtained. This is maybe attributed to the rapid reduction rate of cuprite ions when deposited at a higher etching duration substrate, which tends more Cu_2O to be fill-in between the slender rods and penetrate the space of the adjacent rods. These parameters obtained from the XRD diffraction patterns can be referred to the Table 2.

Table 2 Structural parameters of Cu_2O/TiO_2 HCl-treated samples

Sample	2θ (°)	FWHM, β	Crystallite size, D (nm)	Phase & Plane (hkl)
After etching treatment				
TiO_2 HCl-treated	36.08	0.1574	65.37	Rutile; (101)
After Cu_2O deposition (60 minutes)				
Cu_2O/TiO_2 HCl-treated	36.56	0.2755	35.17	Cuprite; (111)

In Cu_2O crystal structure, each Cu_2O unit cell has a cubic structure where the Cu^+ is linearly connected to two O^{2-} that coordinated in tetrahedral with four Cu^+ ions. It has been demonstrated that the surface energy of Cu_2O is tuneable by various reaction conditions in aqueous copper-based solutions. Such surface energy of an ideal Cu_2O facet is following the order Cu_2O (100) > Cu_2O (110) > Cu_2O (111) [16] and correlating to the atomic arrangement in the crystal structure. Considering the (111) crystal facet is nonpolar/non-reactive and the (100) facet is highly polar; the crystal growth rates are different at the [111] and [100] direction. It can be assumed that when the electrodeposition occurs on the surface of TiO_2-

HCl treated, the Cu_2O particles tend to grow in the direction of the facets that possess a high surface energy. However, the facets with high surface energy are unstable and needs to reduce the energy by means of eliminating these facets, resulting the facets with low surface energy are observed in the diffraction pattern, and this work in accordance with the past literature that have the [111] orientation as the preferential facet [17]. In this case, the surface of Cu_2O (111) has the lowest value of surface energy and is known as the most stable among the surfaces of Cu_2O.

3.3. Morphological Properties

The FE-SEM surface images in Figure 3 reveal the significant differences between the samples before and after etching treatment took place. It was clearly seen that the non-etched TiO_2 nanorods sample consisted of tetragonal pillar shape in geometrical arrangements and distributed evenly on the FTO substrate. The top of the facet looked like a blunt shape and displayed a huge number of step edges, which served as a seed layer for further growth. In certain areas, the gaps between the rods were obviously seen. Such structure inhibited the Cu_2O crystalline structure from growing uniformly on TiO_2 nanorods layer. After being etched for 5 hours, the original TiO_2 nanorods structure turned into split rods. The top blunt structure was vanished and became a hollowed-square top facets, suggesting that the TiO_2 nanorods growth was stopped by the reaction of the HCl treatment.

The Cu_2O layer was deposited in acetate-based solution at pH 12 with deposition time 60 minutes. It was believed that a tiny and wire-like structure of TiO_2 reduces the surface resistivity that enables the Cu_2O growth uniformly. The typical pyramidal structure of Cu_2O was formed in this work and accordance with the previous work which reported that the three-faced pyramids structure could be obtained if the pH level was 11 or the applied potential was -0.45V [18]. Moreover, employing electrolyte at high pH indicates that more OH- ions could be generated thus accelerating the growth rate at the (111) planes to form the three-sided pyramid structure. This may be ascribed to the surface where the Cu_2O was deposited since in their work, the Cu_2O was grown directly onto FTO substrate that having a low resistance. Therefore, it could be demonstrated that the etched TiO_2 nanorods interfacial has an identical profile with FTO substrate that favours to a Cu_2O formation. Even though the Cu_2O is distributed uniformly on TiO_2, which is confirmed by XRD pattern, the structure seemed to have cracks. Such cracks are believed indicating a fast nucleation rate when electrodeposition was conducted at 60 °C of bath temperature.

Figure 4 shows the cross-sectional images give the difference of the film thickness before and after Cu_2O deposition in 60 minutes on etched TiO_2 nanorods substrate. By employing a highly acidic etching treatment to the compact structure, loosened the densely packed TiO_2 nanorods was obtained and decreased the surface resistivity, so that reducing their space and promoting Cu_2O to grow with a typical formation and shape. In addition, the etching treatment did not change the thickness of the TiO_2 nanorods since the thickness of the film is strongly dependent on the molarity of HCl and the etching duration. This work employed low molarity of HCl, therefore the reduction of the film thickness is too small and negligible. In this study, the thickness of TiO_2 nanorods after 5 hours of etching treatment is consistent around ± 3 µm as illustrated in Figure 4.

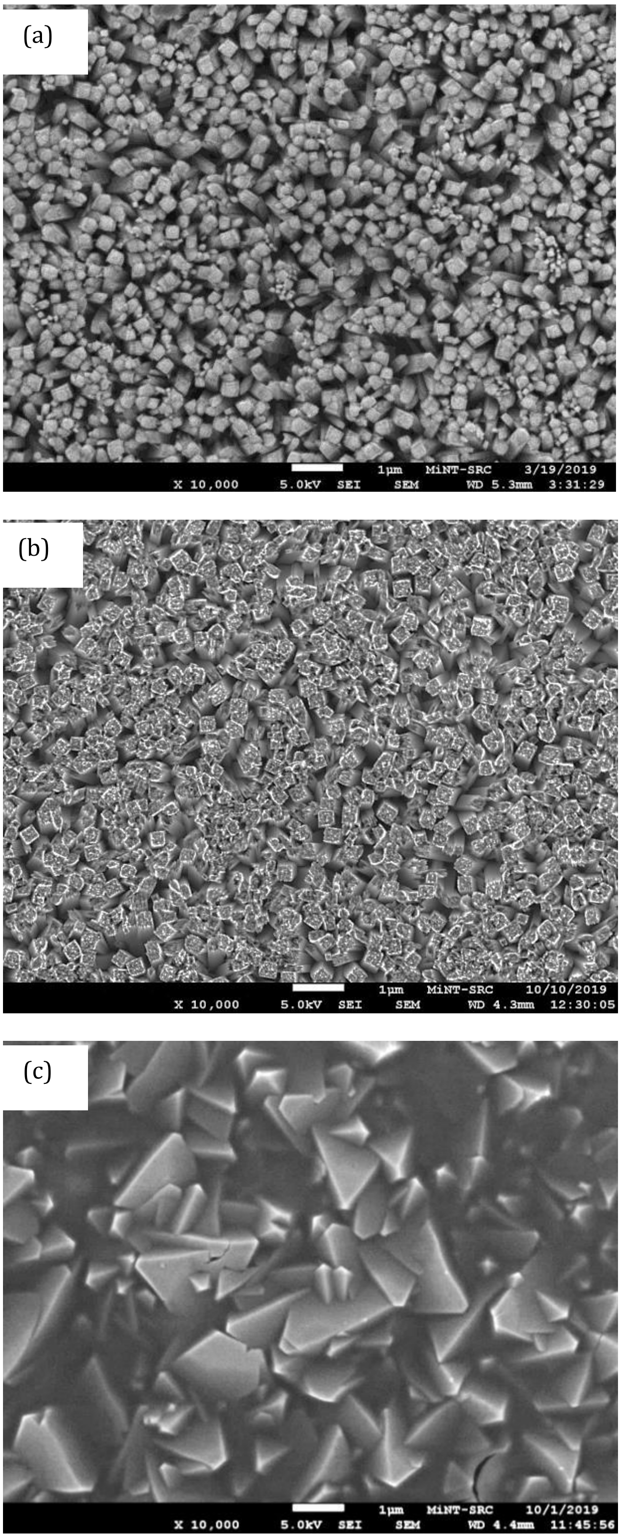

Figure 3. FE-SEM surface images of (a) before etched, (b) after HCl-etched and (c) after Cu_2O deposition under x 10,000 magnification.

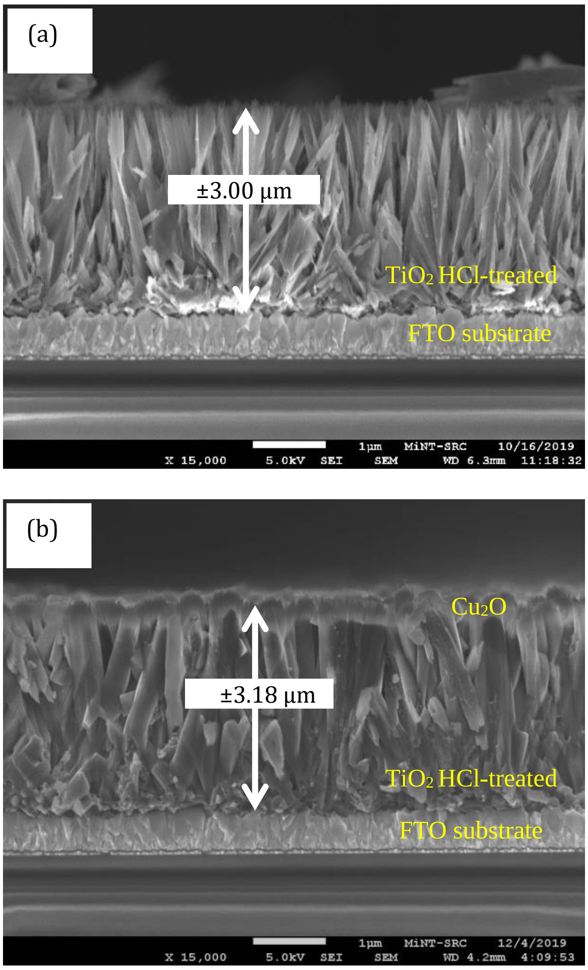

Figure 4. FE-SEM cross-sectional view of the TiO_2 HCl-treated sample (a) before and (b) after Cu_2O deposition.

It is clearly observed that the Cu_2O crystalline filled in the space created by the neighbouring nanorods and subsequently formed the pyramidal structures that were distributed evenly on the top of the samples. Such Cu_2O penetration resembles a connecting layer to enhance the fusion between etched TiO_2 films which is believed could increase the transportation of electrons. The thickness of the sample after Cu_2O deposition is found to be 3.18 µm as shown in Figure 4(b). The film thickness is relatively close to the deposition rate of Cu_2O. It is suggested that the surface of TiO_2 nanorods film is low resistivity since the Cu_2O film exhibited a rapid growth rate in 60 minutes.

3.4. Electrical Properties

The samples were subjected to a four-point probe analysis, which is common method of measuring resistivity, ρ and sheet resistance, R_s of the film synthesized through the film thickness. This was done to examine the electrical properties of the Cu_2O/TiO_2 HCl-treated/FTO film. From the result obtained in Table 3, the ρ and Rs of the etched TiO_2 samples are smaller compared to the Cu_2O that deposited on HCl etched-TiO_2 film. Such low ρ and Rs are the effect from the etching treatment and strongly dependent on the time and high concentration of acidic medium.

Table 3 Electrical properties of Cu_2O/TiO_2 HCl-treated samples

Sample	Resistivity, ρ (Ω.cm)	Sheet resistance, R_s (Ω/sq.)	Film thickness (µm)
Before			
TiO_2 nanorod	0.34	10.9×10^2	±3.00
After HCl treated			
TiO_2 HCl-treated	0.19	6.49×10^2	±3.00
After Cu_2O deposition (60 minutes)			
Cu_2O/TiO_2 HCl-treated	14.40	46.15×10^3	±3.18

However, the ρ and Rs of the Cu_2O after 60 minutes deposition is strongly dependent on the surface area of the HCl-treated TiO_2 substrate. It was observed that the ρ and Rs of Cu_2O increases when the etching time for TiO_2 nanorods elongated within 5 hours. By elevating the etching time, it was expected to increase the surface area of TiO_2 and decrease the surface resistivity. The situation favours to a rapid growth rate of the Cu_2O simultaneously increases the thickness of the Cu_2O deposited film. The increment behaviour of the film thickness can be ascribed to the fast and uniformity Cu_2O growth on the surface of etched-nanorods structure which has become an interfacial layer with low resistance at the surface of the TiO_2 nanorods. However, a higher film thickness of Cu_2O/TiO_2 HCl-etched/FTO as revealed by FE-SEM cross-sectional image in Figure 4 leads to the increasing of ρ and Rs which is limits the solar cell application. In this work, it can be suggested that the ρ and Rs of Cu_2O/TiO_2 HCl-treated/FTO film increase when the etching time in a highly acidic medium in 5 hours, which is demonstrated by a uniformly growth of Cu_2O film.

4. CONCLUSION

TiO_2 nanorods structure has been successfully prepared and modified via two-step hydrothermal method. The HCl treated of TiO_2 film demonstrated as a highly effective interfacial layer. The Cu_2O layer grown uniformly and showed a high crystallinity when depositing on TiO_2 layer. Although the combination of these heterostructure is proven constructed, a lot of works are needed to improve the heterostructure properties to achieve a higher power energy conversion in heterojunction solar cell.

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