

EFFECT OF ANNEALING STRATEGY ON IMPROVED PHOTOACTIVITY OF CUPROUS OXIDE NANOWIRE PREPARED USING FACILE FABRICATION STRATEGY FOR SOLAR WATER SPLITTING

(Kesan Strategi **Penyepuhlindungan** Terhadap Peningkatan Fotoaktiviti Nanowayar Cuprous Oksida Yang Disediakan Menggunakan Cara Mudah Untuk Pembelahan Air Suria)

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Abstract

Cu₂O photocathode such as nanowire (NW) have shown to improve photoactivity than that nanoparticle thin film counterpart. This enhancement is attributed to enhanced photocatalytic reaction due to increase in surface active area and effective radial charge diffusion. However, the photoelectrochemical performance of reported work were rather low which need an improvement prior protection. In this study, Cu₂O nanowire photocathode was fabricated using sequential wet chemical oxidation method and annealing under inert condition. Focusing on annealing step, the transformation of precursor Cu(OH)₂ nanowire to Cu₂O nanowire undergone multistep annealing with a different ramping rate under inert condition. The highest photocurrent was then compared with photocurrent generated from Cu₂O NW prepared with direct annealing strategy. With multistep annealing, the best photoelectrochemical performance was obtained from Cu₂O NW prepared at the highest ramping rate which is 1.2 folds better than that obtained with single step annealing. The photocurrent enhancement obtained in this study was attributed to favourable morphology improving light trapping. Overall, the amplexness of material source, non-toxic, simple fabrication and excellent photocatalytic performance are the pre-requisite to realize solar hydrogen production.

Keywords: cuprous oxide nanowire, photocurrent, water-splitting, hydrogen production

Abstrak

Fotokatod Cu₂O yang berstruktur nano wayar (NW) telah menunjukkan aktiviti foto yang lebih baik berbanding filem nipis. Prestasi fotomangkin yang baik ini disumbang oleh peningkatan luas permukaan yang aktif dan keberkesanan pengaliran cas. Walaubagaimanapun, prestasi fotoelektrokimia yang telah dilaporkan masih lagi rendah dan memerlukan penambahbaikan sebelum penyalutan sebagai perlindungan untuk kestabilan fotokatod. Dalam kajian ini, Cu₂O NW fotokatod telah disintesis menggunakan oksidasi kimia dan pengkalsinan dalam keadaan lengai. Pada peringkat pengkalsinan, transformasi pemula Cu(OH)₂ nanowayar kepada Cu₂O nanowayar telah melalui beberapa langkah pengkalsinan dengan kadar pengkalsinan yang berbeza. Fotoarus yang tertinggi akan dibandingkan dengan fotoarus yang terhasil daripada Cu₂O nanowayar yang disediakan menggunakan pengkalsinan terus. Pada pengkalsinan berperingkat, prestasi fotoelektrokimia yang terbaik didapati daripada Cu₂O NW yang disediakan pada kadar pengkalsinan yang paling tinggi iaitu 1.2 kali ganda lebih baik berbanding yang didapati daripada pengkalsinan terus. Peningkatan fotoarus yang terhasil daripada kajian ini telah disumbangkan oleh kesan morfologi bahan yang berkeupayaan menyerap cahaya secara efektif. Keseluruhannya, keberadaan sumber bahan yang mencukupi, tidak toksik, cara penyediaan yang mudah, serta prestasi fotomangkin yang bagus adalah keperluan untuk merealisasikan penghasilan hidrogen dari tenaga suria.

Kata kunci: nanowayar kuprous oksida, fotoarus, pembelahan air, penghasilan hidrogen

Introduction

The photocatalytic performance of Cu_2O photocathode for photoelectrochemical application can be enhanced by nanostructuring owing to its high surface area for photocatalytic reaction and alleviated issue of mismatch between the intrinsic carrier diffusion length [1, 2] and the light absorption depth near the band gap [3]. This single metal oxide was theoretically estimated to produce approximately -15 mA/cm^2 and photoconversion efficiency of 18% based on the AM 1.5 spectrum [4]. As photocathode, recent research trend has been attempts to fabricate the photocathode with nanowire (NW) arrays film [5-8] and stabilize it using facile technique and inexpensive protective material, respectively [4, 9-12]. Prior to stabilization, priority should be given to improve the photocurrent generation that can be tapped from the photoharvester of Cu_2O film. This step is crucial to compensate photocurrent reduction which might be due to poor charge transportation between overlayers or any deleterious effect of the film after the coating treatment [9, 13-15]. Cu_2O NW can be fabricated using sequential wet chemical oxidation method (WCOM) [1, 6, 11, 16] followed by annealing under inert condition as one of the method which promotes facility and high quality. This method is initiated with the fabrication of $\text{Cu}(\text{OH})_2$ NW as precursor using WCOM [17] before transforming to Cu_2O NW through annealing under inert condition. Focusing on the annealing process, the transformation of the precursor to Cu_2O NW involved dehydration and deoxidization step [17, 18]. Therefore it needs a multistep of annealing to provide each step with a complete transformation from $\text{Cu}(\text{OH})_2$ to CuO through dehydration and ultimately CuO to Cu_2O through deoxidization.

Through literature survey on PEC application, there was only one single study which we know of following similar annealing strategy for Cu_2O NW fabrication from $\text{Cu}(\text{OH})_2$ NW precursor [19]. However, this study only managed to achieve photocurrent of -2.05 mA/cm^2 at 0.265 V vs. RHE which was produced from the sample annealed at 700°C for 2 hours. The low photocurrent could be due to diminishing NW structure at high annealing temperature, thus decreased surface active area for photocatalytic reaction. Other reported studies with similar material and strategy deemed to practise a direct annealing since no details were mentioned on annealing step [5, 6, 8, 12, 16]. As far as photocurrent generation is concerned, the highest photocurrent ever reported for bare Cu_2O from WCOM was -4.07 mA/cm^2 at 0 V vs. RHE. This PEC performance was achieved using WCOM and direct annealing at 500°C for 2 hours under Argon flow [10]. Based on the maximum theoretical measurement of photocurrent for Cu_2O photocathode mentioned above, there is indeed more room for improvement.

Therefore, in this study, an annealing with multistep strategy was used to affect an improved Cu_2O NW photocathode with excellent PEC performance. Since the effect of annealing temperature [5, 10], and holding time [8] were well studied, hence we investigated the effect of multistep ramping rate at 500°C for 2 hours. For comparison, a direct annealing was conducted under similar annealing parameter that affect the highest photocurrent.

Materials and Methods

The fabrication of $\text{Cu}(\text{OH})_2$ NW

In most recent studies, $\text{Cu}(\text{OH})_2$ NW was prepared using an established method proposed by Zhang et. al. [17]. However, in this study, the growth solution was modified by the addition of NH_3 . Briefly, a sheet of copper foil as substrate of 1 cm^2 was cleaned in acetone, ethanol, and double distilled water (ddH_2O) for 5 minutes each, consecutively. The wet Cu foils were then dried with nitrogen flow prior to immersion in growth solution. The growth solution composed of 2.67 M NaOH (Amreck), 0.133 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Sigma), and 4.26% NH_3 (Merck), were dissolved in ddH_2O as reaction media. After 25 minutes of reaction, blue film appeared covering the substrate indicating the growth of $\text{Cu}(\text{OH})_2$ NW. Then, the grown film was rinsed with ddH_2O and dried in air.

The conversion of $\text{Cu}(\text{OH})_2$ NW to Cu_2O NW

The as-prepared $\text{Cu}(\text{OH})_2$ NW film was then subjected for annealing to be converted to Cu_2O NW under N_2 flow. Three levels of ramping rate at 1 , 3 , and 5°C/min were carried out to reach final temperature of 500°C for 2 hours. Routinely, the furnace was first evacuated with vacuum and followed by nitrogen sparging alternately for 3 cycles. Then, from room temperature, the furnace was first raised to 120°C with 5°C/min ramping rate and held at 120°C

for 60 minutes before ramped up to 180 °C for 1 hour and held for another 1 hour. With different ramping rate as mentioned, the temperature was finally raised to 500 °C and held for another 2 hours before cooling down. For comparison on PEC performance, a direct annealing (without multistep) was conducted at the pre-determined ramping rate under similar annealing condition. For simplicity, hereafter, the Cu₂O NW sample prepared with multistep annealing at 1, 3, and 5 °C/min ramping rate were denoted as Cu₂O-(1 °C/min), Cu₂O-(3 °C/min), and Cu₂O-(5 °C/min), respectively. Whereas sample labelled with Cu₂O-(5 °C/min)(D.A) stands for Cu₂O NW which prepared with direct annealing strategy at 5 °C/min.

Structural characterization

The morphology of the samples was characterized using a Variable Pressure Scanning Electron Microscope (VPSEM). The crystallinity of the samples were determined by X-ray diffractometer (XRD) (Bruker D8 Advance), using Cu K α radiation. Whereas, the UV-vis diffuse reflectance spectra were determined with a spectrophotometer (Perkin Elmer, Lambda 950).

Photoelectrochemical measurement

The photoresponse of the samples were measured using three electrodes configuration contained in a photocell with expose area of 0.196 cm². The fabricated photoelectrode was assigned as working electrode, Ag/AgCl as reference electrode, and platinum as counter electrode. Cu tape was connected to photoelectrode sample and clamped before it is filled with electrolyte. Those electrodes were immersed in 0.5 M Na₂SO₄ solution which was purged with Argon for 10 minutes prior to measurement. The photocurrent measurement was acquired under AM 1.5 Xenon light irradiation at 100 mW/cm². The photocurrent density was then determined as a result of subtraction between light and dark current and divided by the sample's exposed area.

Results and Discussion

Characterization of Cu₂O NW film

The transformation of Cu(OH)₂ NW to Cu₂O NW depicts a morphology changes from a straight-standing Cu(OH)₂ NW to bendy and segmented Cu₂O NW (Figure 1). The changes can be seen started at 180 °C (Figure 1b) where a straight NW of Cu(OH)₂ NW was appeared bendy and the films turned black (insert 1b). As temperature increased to 500 °C at different ramping rate and held for 2 hours, a dramatic change on the NW strand was noticed (Figure 1c, 1d, and 1e) indicating Cu₂O NW was produced as evidenced from XRD analysis Figure 2. It was reported that the curly and bendy NW after annealing was due to the stress of phase changes resulted from oxygen separation from the lattice of CuO [8].

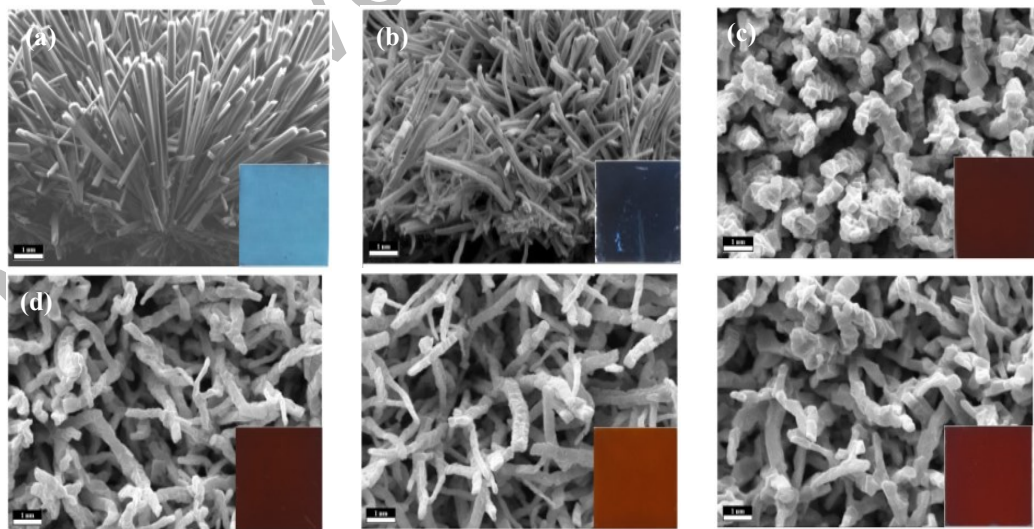


Figure 1. SEM images of a) Cu(OH)₂ NW, b) CuO NW, Cu₂O NW prepared at multistep annealing with different ramping rate at c) 1 °C/min, d) 3 °C/min, e) 5 °C/min, and f) without multistep Cu₂O NW-(5 °C/min) (D.A)

The phase transformation from CuO to Cu₂O is explainable with deoxidization reaction where oxygen molecules was removed from the CuO lattice and reducing the ionic state from 2 to 1 becoming Cu₂O [17]. Along with morphology changes, the NW dimension also changed accordingly as tabulated in Table 1.

Table 1. The dimension of nanowire before and after annealing measured using ImageJ software

Samples	Length (μm)	Width (μm)
Cu(OH) ₂ NW	5.60 ± 0.20	0.40 ± 0.02
Cu ₂ O-(1 °C/min)	2.72 ± 0.14	0.82 ± 0.14
Cu ₂ O-(3 °C/min)	3.12 ± 0.09	0.45 ± 0.01
Cu ₂ O-(5 °C/min)	4.07 ± 0.08	0.39 ± 0.08
Cu ₂ O-(5 °C/min)(D.A)	3.33 ± 0.07	0.56 ± 0.04

The results obtained here can be concluded that, the length and width of NW arrays were shortened and widen as the ramping rate decreased. This observation is attributed to agglomeration of NW structure affected by long annealing time imposed by the lowest ramping rate. A long annealing time induced the increase in crystal size which is in agreement with reported study [8]. On the other hand, samples annealed at higher ramping rate has shorter annealing time and were not severely impacted by agglomeration, hence appeared to be the longest NW. Although Cu₂O-(5 °C/min)(D.A) sample was prepared with the shortest annealing time, its NW length is shorter than that measured for Cu₂O-(5 °C/min). This shows that during the multisteps annealing the different holding time at different temperatures affected the agglomeration rate differently than during direct annealing. Furthermore, it is reported that the curly and bendy NW after annealing was due to the stress of phase changes resulted from oxygen separation from the lattice of CuO [8].

In Figure 2, an overlayer of XRD pattern of the samples pre and post annealing are displayed. A distinct XRD pattern of each sample reflecting a complete transformation from Cu to Cu(OH)₂, CuO and subsequently to Cu₂O after annealing. Cu₂O is known with dominant peak of 111 phase which claimed to be responsible for good PEC performance [5, 20]. This particular peak has increased in intensity as the ramping rate decreased which remarked an improved crystallinity with longer annealing time (Figure 2). Contrastingly, the Cu₂O-(5 °C/min)(D.A) has shown a higher peak intensity than that obtained by Cu₂O-(5 °C/min). The peculiar results on NW dimension and crystallinity demonstrated by Cu₂O-(5 °C/min)(D.A) sample might be clarified through the study of effect of annealing temperature on dominant peak intensity through direct annealing strategy.

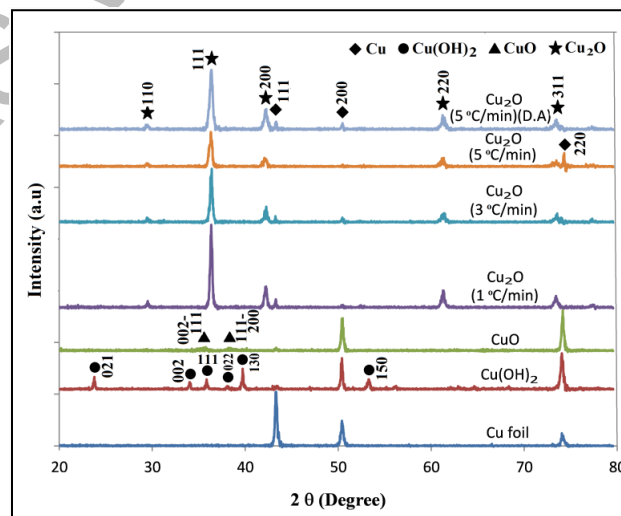


Figure 2. The overlayer of XRD pattern of samples pre and post annealing

The photoabsorption of the annealed samples were measured using diffuse reflectance spectrophotometry (Figure 3a). The higher reflectance indicates lower light absorption. Therefore, in this study, Cu₂O-(5 °C/min) has the higher capacity in absorbing light than Cu₂O-(1 °C/min) specifically within 300 – 500 nm light spectrum frame. This observation has the correlation with the morphology which structured at different ramping rate. As mentioned earlier, short and bulky NW arrays were made of large crystal which featured with low surface area to volume ratio. Dimensionally, it did not encourage high light absorption capacity. Long and slim NW arrays, on the other hand, were made of small crystal which structured at relatively shorter annealing time, thus enhancing light trapping efficiency. These observations are in line with the previous reported study with similar research material and strategy [8]. In order to determine the band gap of each Cu₂O NW sample, Kubelka Munk-plotting function was used against band gap energy [21]. From the K-M plotting (Figure 3b), a very close band gap for all samples were extrapolated to be 2.05 ± 0.01 eV. The obtained band gap values are consistent with reported value and within the favourable band gap frame (1.8-2.1 eV) for PEC application as suggested by Murphy et al. [22].

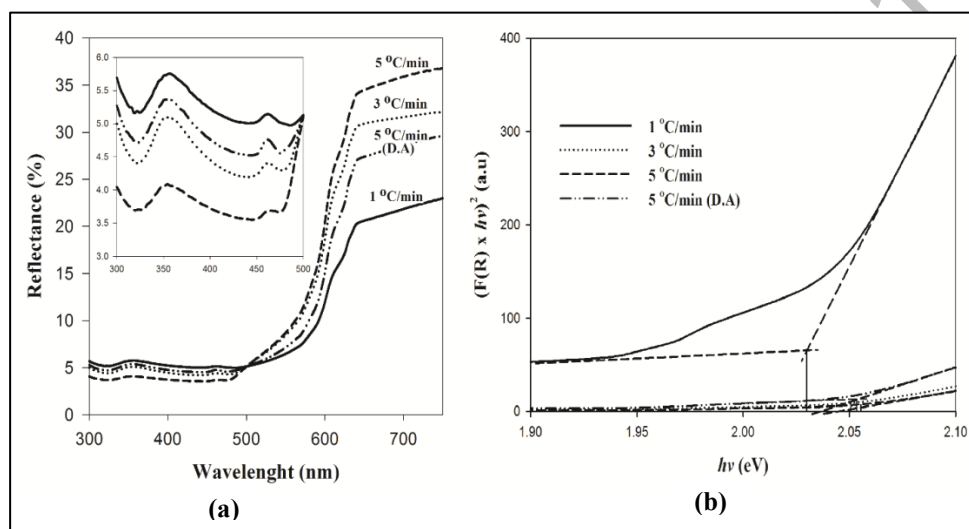


Figure 3. Diffuse reflectance spectra of a) Cu₂O NW prepared at different ramping rate and annealing step; the insert shows the light reflectance value within a light spectrum frame, b) the corresponding Kubelka-Munk plot for the Cu₂O NW-(1°C/min), Cu₂O NW-(3°C/min), and Cu₂O NW-(5°C/min), and Cu₂O NW-(5 °C/min)(D.A)

Photocurrent measurement

The photocurrent appears to be influenced by the morphology of the NW which was affected by the ramping rate (Figure 2). A longer and thinner NW produced by a higher ramping rate (shorter time) enhanced photocurrent. Although the XRD peak intensity reduced with the higher ramping rate (shorter annealing time), this does not seem to reduce the photocurrent. Therefore, the NW morphology appears to have more effect on the photocurrent than the XRD peak intensity. This is shown by Cu₂O-(5 °C/min) produced the highest photocurrent which benefitted from the long and slimmer NW which concomitantly provides high surface active area [23, 24], and improved radial charge diffusion for a better photocatalytic reaction [23, 25]. As the band gaps are very similar (Figure 3b), the photocurrent appears to be influenced solely by the morphology of the NW. Whereas, a lower ramping rate (longer annealing time) produced shorter and wider NW resulting in lower photocurrent. Even though the direct annealing strategy (Cu₂O-(5 °C/min)(D.A)) has the shortest annealing time, but the photocurrent produced was significantly lower than that obtained by the sample Cu₂O-(5 °C/min). This can also be observed from the NW morphology as well, where Cu₂O-(5 °C/min)(D.A) has shorter and wider NW compared to Cu₂O-(5 °C/min). Furthermore, Cu₂O-(5 °C/min)(D.A) reflects light higher than Cu₂O-(5 °C/min)(D.A) which explained the photocurrent reduction as shown in Figure 4. Eventhough Cu₂O-(5 °C/min)(DA) was prepared at the shortest annealing time, however the multistep annealing used in the Cu₂O-(5 °C/min) preparation improved the NW morphology which resulted in enhanced

photocurrent. This result suggested that multistep annealing is critical to affect complete phase transformation during the course of annealing.

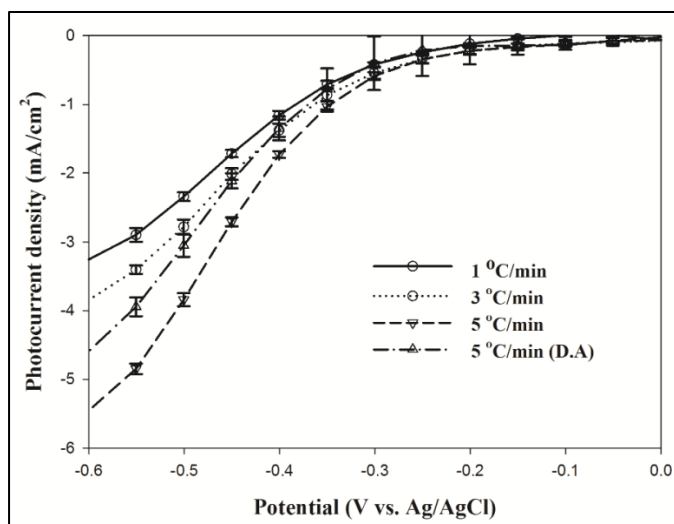


Figure 4. Photocurrent measurement generated from Cu₂O annealed at different ramping rate and annealing step

Conclusion

In this study, the photoactivity of Cu₂O NW was markedly influenced by the effect of ramping rate which found to be analogous with the effect of annealing time. With longer and slimmer NW, Cu₂O-(5 °C/min) sample exhibited the highest photoabsorption and photocatalytic activity, thus resulted with the highest photocurrent generation relative to the other Cu₂O sample. This study also suggesting that a multistep annealing is necessary to prepare a good quality of Cu₂O NW photocathode. Technically, this low cost and simple fabrication technique for Cu₂O NW photocathode was adequate to produce a highly efficient photoelectrode for PEC system. The next step is to stabilize the Cu₂O NW from photocorrosion problem which remain the biggest challenge.

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