Tunable morphology and band gap alteration of CuO-ZnO nanostructures based photocathode for solar photoelectrochemical cells

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Abstract

A homogeneous CuO-ZnO nanostructure with tunable morphology and optical band structure is successfully synthesized via a hydrothermal method under the different dopant mole ratios of Cu. The robust correlation between the crystallite size, surface morphology, optical band gap alteration of the synthesized CuO-ZnO and its performance in photoelectrochemical (PEC) activity are investigated and compared to the reference ZnO based photocathode. In this report, it is found that the morphology of hexagonal ZnO nanorod is changed to nanosheet and vertically align CuO-ZnO based nanograss after the Cu incorporation. This result is mainly due to the composition phase change after the excessive incorporation of Cu metal into ZnO lattice. Furthermore, the optical band gap of the sample also presented a bathochromic shifted after the Cu insertion. The measurements on PEC activity of CuO-ZnO nanostructure was performed under the irradiation of a 100 mWcm⁻² Xenon light in 0.5M Na₂SO₄ electrolyte. Among the sample, 0 Zn:1 Cu exhibited a highest photocurrent density which is 5 fold as compared to its reference ZnO samples. This finding could be due to the highest surface active area and lowest optical energy band gap in the 0 Zn:1 Cu nanograss that eventually contributes to a high free electron density that facilitates the charge transport in the photoelectrochemical cells. This novel approach could provide an alternative to the future solar hydrogenation application.

1. Introduction

Numerous researches have been carried out to investigate the potential of zinc oxide (ZnO) for various applications such as photoelectrochemical (PEC) cells, solar cells, gas sensors, and light-emitting diodes [1–5]. In the PEC cells, the ZnO photoanode provides an efficient and cost-effective alternative for the conversion of widely available solar energy into chemical fuel on a scale comparable to worldwide energy demands [6, 7]. Its superior electron mobility as well as photo-corrosion resistance make it a promising choice for the PEC cells [8, 9]. However, its wide band gap (Eg = 3.37 eV) limits its absorbance spectrum to only 4% in the ultraviolet range of solar spectrum away from the Sun’s peak at ~500 nm.

Recently, the incorporation of metal dopants has been studied, to improve the inherent limitations of ZnO [10, 11]. Transition metal-based dopants have been reported as potential materials used in altering the characteristics of ZnO nanorods (NRs), particularly, shifting the optical absorption spectra of the host materials.
to the visible light region [12–14]. One of the most extensive dopants is copper (Cu). The Cu is known to be an active and cost-effective co-catalyst. It has a high degree of compatibility with the ZnO owing to its similar electronic band structure and physical properties [15]. Therefore, the Cu is selected in this study, aiming to improve the interfacial charge-transfer kinetics and results in a significant improvement of the ZnO NRs photoactivities. The effects of Cu doping in the morphological and optical properties of ZnO crystal structures has been studied [16–19]. Shaislamov et al reported the fabrication of CuO/ZnO nanorod/nanobranch photocathodes by using template-assisted electrodeposition and hydrothermal methods. They proved that the PEC performance and stability are greatly correlated with the density and length of the ZnO NR branches. The maximum photocurrent density of $–1.4$ mA cm$^{-2}$ (at $–0.5$ V) for CuO NR electrode was measured, which indicated a higher value compared to $–0.9$ mA cm$^{-2}$ for CuO/ZnO NR electrode [20]. This structure was modified by Thuy et al using a WO$_3$ and CuO nanobranch and improvement of PEC performance was achieved. The photocurrent of 1.28 mA cm$^{-2}$ at 1.23 V was reported for ZnO with WO$_3$ nanobranches while CuO nanobranches represented a superior value of 2.49 mA cm$^{-2}$ [21]. Liu et al also prepared a CuO/ZnO p–n heterojunction photoanode by chemical and annealing processes, and the maximum photocurrent density of 0.97 mA cm$^{-2}$ at 1.23 V was reported [22]. Prabhu et al have synthesized CuO/ZnO p–n heterojunction nanostructures via the hydrothermal method. They recorded the photocurrent density of $–0.003$ mA cm$^{-2}$ at $–0.3$ V [23]. The effects of Cu$_2$O nanocube on the PEC performance of ZnO films via the electrochemical method were investigated by Qadir & Erdogan, and the highest PEC performance of 3 mA cm$^{-2}$ was reported by this group [24]. Facial and low-cost fabrication methods as well as high-performance devices are the essence in the literature. In this regard, we present a respected high-performance device in a very cost-effective approach.

In this study, the ZnO NRs and CuO-ZnO nanostructures were synthesized by using the hydrothermal method in various Cu molar ratios, and their structural and optical properties were investigated. A noteworthy transition in structural properties led to a change of band gap, which resulted in improved absorption. Furthermore, the usage of the as synthesized electrodes as an n-type photoanode and p-type photocathode in photo-electrochemical reactions was also investigated.

2. Material and method

2.1. Synthesis of CuO–ZnO nanostructures

Firstly, the Fluorine-doped tin oxide (FTO) substrates were cleaned by sonicating in methanol and acetone for a duration of 10 min each and subsequently rinsed with deionized (DI) water. The substrates were then dried using nitrogen (N$_2$) gas. Radio frequency (RF) magnetron sputtering (Kurt J Lesker PVD-75) was used to deposit a ZnO based thin film. A Zn metal target with a purity of >99.99% (PO 1210097/KS Aci Alloys Inc.) was used. Sputter power for the process was fixed at 150 W and the deposition was carried out for 30 min at ambient temperature. Oxygen (O$_2$) gas was purged to the system during the sputtering process to transform the deposited Zn nanoparticles into ZnO. The colour of the deposited films was found to be translucent. The FTO substrates were then annealed at 350 °C for 2 h in an ambient environment to produce a 200 nm thick seed layer. In order to grow a ZnO nanorod, the precursor solution was prepared by dissolving 40 mM of zinc nitrate hexahydrate Zn(NO$_3$)$_2$·6H$_2$O and hexamethylenetetramine (HMT) (CH$_2$)$_6$N$_2$ (from Sigma-Aldrich) respectively in 100 ml of DI water. The solution was stirred continuously for 50 min at room temperature and then transferred to a Teflon-lined autoclave. The autoclave is then sealed and heated at 95 °C for 5 h in a laboratory oven. After that, the samples were rinsed with DI water and then dried at 100 °C for 30 min. Lastly, all of the samples were annealed in a N$_2$ gas purged vacuum furnace (OTF-1200X) at 500 °C for 2 h. A similar procedure was carried out to prepare CuO–ZnO nanostructures at 4 different molar ratios of Zn to Cu (3:1, 1:1, 1:3, 0:1) on the ZnO seed layer. The precursor solution that consisted of zinc acetate (Zn(CH$_3$COO)$_2$·2H$_2$O), HMT and copper sulphate pentahydrate (CuSO$_4$·5H$_2$O) (Sigma-Aldrich) was used.

2.2. Characterization of ZnO NR and CuO-ZnO nanostructures

X-ray diffractogram (XRD) was used to determine the crystalline structure of the fabricated ZnO NRs and CuO–ZnO nanostructures. The detail analyses on microstrain and crystallite size was performed using Scherrer’s formula. FESEM was used to study the surface morphology of the samples whereas EDX was carried out to investigate the presence and distribution of elements on the surface. Optical transmission spectra and optical band structure for all samples were obtained via UV–vis spectroscopy with wavelengths varying between 200–1000 nm and analysed using the Tauc relation.

2.3. Photoelectrochemical activity measurements

The photoreponse of the samples were measured using a three-electrode system enclosed in a customized photocell. The sample was used as the working electrode and was attached to a photocell bearing with an active
(exposed) area of 0.196 cm$^2$. A platinum wire and Ag/AgCl-saturated in 3M KCl-electrode was used as the counter electrode and reference electrode, respectively. Before the device analysis, the system was purged with N$_2$ gas for 30 min. During the testing, the electrodes were immersed in 0.5M of Na$_2$SO$_4$ electrolyte. The measurements on photoelectrical activity of the system were conducted via linear scan voltammetry (Ametek Versastat4) with a scan rate of 0.05 Vs$^{-1}$ under 100 mWcm$^{-2}$ xenon light irradiation.

3. Results and discussion

The structural properties of ZnO nanorods and CuO–ZnO nanostructure were analysed via x-ray diffraction as presented in figure 1. For pristine ZnO NRs, the obtained XRD patterns in this study are in agreement with the standard spectrum documented in JCPDS card No. 01-076-0704 indicating hexagonal structures. Five peaks are observed at 31.74°, 34.38°, 36.22, 47.48°, and 56.54° that corresponding to (100), (002), (101), (102) and (110) preferred orientations. As the Cu ratio starts to increase, the intensity of ZnO peaks decreases drastically and diminishes completely for 1:1, 1:3 and 0:1 Zn:Cu samples. The emergence of CuO and Cu$_2$O peaks is detected harmonizing with JCPDS of No. 00-045-0937 (monoclinic) and No. 01-071-3645 (cubic), respectively. These results confirmed the successfulness of Cu atom diffusion in the ZnO lattice. The incorporation of Cu dopants into the ZnO crystal lattice decreases the film’s crystallinity due to excessive formation of crystallographic defects. In the 1:1 sample, the dominant (−111) and (002) CuO planes together sharing the highest peak intensity at 35.50°. This sample has the low intensity (111) Cu$_2$O plane at 36.43° as well. From 1:1 to 0:1 samples, the intensity of the CuO peaks decreases while the Cu$_2$O peaks have an increment in their intensities similar to the literature [25]. It was reported that the increase in Cu content may cause an increase in carrier concentration and mobility in the conduction band of ZnO, which solely depends on crystallographic properties [26]. Using the Debye–Scherrer equation (1), the average crystallite size, D of ZnO and CuO-ZnO nanostructure are calculated.

$$D = \frac{0.9 \lambda}{\beta_{hkl} \cos \theta}$$

where $\lambda$ is the wavelength of the incident x-ray beam (1.541 Å), $\beta_{hkl}$ is the Bragg’s diffraction angle and $\beta_{hkl}$ is the full-width at half-maximum for the dominant peaks. It was observed that the peak intensity is likely to have adverse impact on the D in our experiment and superior D values are expected despite having the inferior intensities [27]. For instance, The D for (111) Cu$_2$O planes in 1:1, 1:3, and 0:1 samples are obtained 40.1, 32.09, and 24.26 nm, respectively. This result is aligned to the previous claim that the excessive insertion of larger size of Cu atom could induce a lattice expansion in the ZnO lattice. These internal stresses in crystal lattices lead to cause peak broadening in XRD diffraction patterns [28]. It is noteworthy that the (002) ZnO peak for 1:0 and 3:1 samples represents a close value of 44.53 and 44.46 nm while (002) and (−111) CuO peaks for 1:1 are intended to be 26.2 nm.

Figure 2 shows the FESEM micrographs of the as-grown ZnO nanorods and CuO–ZnO nanostructure prepared from different molar ratios. From the figure 2, it was found that a uniformly and well-oriented one.
dimensional ZnO nanorods were successfully grown on the FTO substrate. The grown ZnO NRs presented a hexagonal-shaped with diameter and length of (101.25) nm and (2) μm, respectively. After the copper incorporation, it was found that the morphology of the nanorod was changed to the irregular hexagonal nanosheet sample. When the Cu molar ratio is further increased to 3, the solid nanosheet sample was transformed into a smaller nanosheet with approximately thickness length of (165.708) nm and (1217.04) nm.

To further confirm the mechanistic formation of Cu incorporated ZnO nanostructure, the sample without the ZnO compound was prepared and labeled as 0:1 Zn: Cu. It is observed that a well-aligned porous nanograss like structure was formed on the FTO substrate with diameter of (42.49) nm and length of (729.122) nm. It is believed that the Cu nanoparticle was self-assembled along its’ metastable plane of (111) during the crystal growth process [29]. This process became dominant in the existence of HMT which acted as a surface capping agent on the side walls of CuO and eventually promote the crystal growth along the c-axis [30].

For the formation of ZnO nanorod, the similar mechanism can be considered as reported in our previous work [31]. After the Cu is incorporate into the ZnO crystal lattice via the hydrothermal approach, the Cu precursor will react with the ZnO nanorod to form a CuO-ZnO nanostructure. The following phase transformation of the crystal can be considered: (a) Firstly, the Cu ion will dissolve from its precursor source of copper sulphate pentahydrate (CuSO4.5H2O); (b) The Cu ion will adsorb on the surface of Zn(OH)2; (c) When the HMT is added into the growth solution, the Cu2+ will reduce to form a Cu+ and simultaneously reduce the Zn(OH)2 to ZnO; (d) Finally, the Cu+ will react with the ZnO and CuO-ZnO are formed. When the molar ratio of Cu is increasing, the crystal growth rate of CuO is became predominate and lead to the reduction of hexagonal characteristic of ZnO. This result is associated with the FESEM images which showed the crystal transform from hexagonal structure (High molar ratio of Zn) to nanograss like structure (High molar ratio of Cu). A large surface to volume ratio in CuO-ZnO nanostructures can have significant contributions towards improving accessibility of surface oxygen vacancies and ultimately facilitating surface activity [32]. It is believed that the CuO-ZnO samples would exhibit improved surface activity in photocatalytic applications due to the high surface-to-volume ratio.

The elemental composition and distribution of the Cu modified ZnO sample was evaluated using the EDX point and mapping analysis. The data was tabulated in table 1 and figure 3. From the spectra, there are three elements namely Zn, O and Cu was detected in the sample. There is no impurity was recorded, signify the high purity state in the fabricated sample. The weight percent of the Cu element is found to be increased with the dopant concentration. In the another note, the wt% of Zn element was decreased from 30.97 in 3:1 Zn: Cu mole ratio to 9.09 in 1:3 Zn: Cu mole ratio. This result confirms the successful growth of Zn: Cu Nanostructure. The distribution of the element was further proved by the insert mapping analysis. In overall, it can be observed that the sample possess a homogeneous Zn and Cu distribution. This result is in accordance to the claim as stated in the XRD and FESEM analysis.

Figure 4 illustrates the absorbance spectra of pristine ZnO and CuO-ZnO samples. CuO-ZnO samples demonstrated photon absorptions in both UV and visible light regions whereas pristine ZnO NRs had an absorption peak at 351 nm which is analogous to its direct energy bandgap. The samples with Zn:Cu ratios of (3:1, 1:1, 1:3, 0:1) Zn:Cu exhibited absorption peaks at (351, 388, 390, 402) nm respectively. This finding suggests
possibilities for CuO-ZnO nanostructure to be applied as photosensitizers in wide-bandgap semiconductor applications. Moreover, the peaks demonstrated a finite positive shift due to the presence of Cu in the ZnO crystal structure. This indicates a change in the electronic band structure of ZnO to one that is previously observed in multimetal oxides [33]. Additionally, optical energy band gaps of the prepared samples were determined based on Tauc plots of $\omega(h\nu)^{1/2}$ versus photon energy, considering indirect allowed transitions. Apparently, it is seen in the inset of figure 4 that the band gap energy of CuO-ZnO nanostructures decreases as mole ratio increases with the lowest band gap value of 2.7 eV obtained for sample prepared at the highest mole ratios of 0:1 (Zn:Cu). Note that 0:1 sample does not consist entirely of CuO due to the presence of ZnO seed layer underneath. From the illustration, it can be observed that increased Cu doping has a positive effect on narrowing the bandgap of ZnO NRs due to the Burstein Moss effect. These results also showed a higher concentration of

Figure 3. The EDX spectra for CuO-ZnO sample.

Figure 4. UV–vis absorption spectra and Tauc plot for ZnO NR and CuO-ZnO nanostructure prepared from different molar ratios.
free charge carriers in the 1 Zn:3 Cu, 0 Zn:3 Cu samples and their potential used as photocathode in photoelectrochemical cell.

The photocurrent density of pristine ZnO NRs and various mole ratios of CuO-ZnO nanostructure was measured to investigate the effect of Cu doping on the photoelectrochemical activities of the samples. The photocurrent of pristine ZnO NR samples increased with an increase in applied potential, suggesting photoanodic behaviour or n-type conductivity. A reduction in the photocurrent of CuO-ZnO samples was observed following the increase in applied potential, which implies photocathodic behaviour (p-type conductivity). As illustrated in figure 5 all CuO-ZnO samples exhibited significantly higher photocurrent densities compared to previous reports [13, 34, 35]. Furthermore, values for photocurrent density increased proportionately with Cu doping concentrations up to optimal molar ratios of 1 Zn:3 Cu, 0 Zn:1 Cu.

It was found that higher photocurrents were detected for all CuO-ZnO samples compared to their pristine counterparts. This observation might be caused by the greater photocatalytic surface area following a high optical absorption [36, 37]. This finding is in agreement with results from previous reports [38, 39]. Furthermore, improvements in photocurrent density of CuO-ZnO samples can be correlated to findings from UV–vis, where CuO-ZnO samples had higher light absorption intensities compared to pristine ZnO NRs [40]. Enhanced photocurrent generation is believed to be caused by the presence of supplemental reactive sites and improved charge carrier diffusion at the electrode/electrolyte interface [34]. In addition, the aforementioned phenomenon can also be caused by the incorporation of deep-acceptors (Cu) and the amorphous nature of the particles formed [41, 42]. Evidence also shows that the specific crystal plane and structure of Cu2O plays a role in enhancing the current density in devices, resulting in superior photoelectrochemical performance [43].

Moreover, literature surveys revealed that CuO-ZnO nanostructure with higher crystallinity tend to achieve optical absorption in the visible light spectrum, enhancing device performance. As such, further in-depth analyses are necessary for investigating tunable photoresponse of CuO-ZnO nanostructure.

### 4. Conclusions

In summary, a hexagonal shaped ZnO nanorods and CuO-ZnO nanostructure were synthesized using a hydrothermal method under different molar ratio of Cu: Zn. It is observed that the CuO-ZnO nanostructure possesses a phase transformation from hexagonal wurtzite ZnO structure to monoclinic CuO structure, and...
supported by the high strain value. The morphology of the sample was also found to be changed from nanorod nanosheet. Furthermore, the optical band gap of the sample also presented a bathochromic shifted after the Cu insertion. The measurements on PEC activity of CuO-ZnO nanosheet. Furthermore, the optical band gap of the sample also presented a bathochromic shifted after the Cu insertion. The measurements on PEC activity of CuO-ZnO nanosheets was performed under the irradiation of a 100mWcm⁻² Xenon light in 0.5M Na₂SO₄ electrolyte. Among the samples, 1 Zn:3 Cu, and 0 Zn:1 Cu exhibited a highest photocurrent density which is 5 fold as compared to its reference ZnO samples. This finding could be due to the highest surface active area and lowest optical energy band gap in the 1 Zn:3 Cu nanosheet and the 0 Zn:1 Cu nanoglass like structure that eventually contributes to a high free electron density that facilitates the charge transport in the photoelectrochemical cells. The current study also revealed that doping ZnO with Cu offered complementary chemical features that lead to the distinctive reaction pathways which are not observed in ZnO individually.

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