Research Article

Easy Formation of Nanodisk-Dendritic ZnO Film via Controlled Electrodeposition Process

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A facile electrodeposition synthesis was introduced to prepare the nanodisk-dendritic ZnO film using a mixture solution of zinc chloride (ZnCl₂) with potassium chloride (KCl) that acted as a directing agent. This study aims to determine the best photoelectrochemical response for solar-induced water splitting. Based on our results obtained, it was found that an average diagonal of nanodisk was approximately 1.70 μm with the thickness of ≈ 150 nm that was successfully grown on the surface of substrate. The photocatalytic and photoelectrochemical responses of the resultant wurtzite type based-nanodisk-dendrite ZnO film as compared to the as-prepared ZnO film were monitored and evaluated. A photocurrent density of 19.87 mA/cm² under ultraviolet rays and 14.05 mA/cm² under visible light (500 nm) was recorded for the newly developed nanodisk-dendritic ZnO thin film. It was believed that nanodisk-dendritic ZnO film can harvest more incident photons from the illumination to generate more photoinduced charge carriers to trigger the photocatalytic and photoelectrochemical reactions. Moreover, strong light scattering effects and high specific surface area of 2D nanostructures aid in the incident light absorption from any direction.

1. Introduction

Behind the rapid development of social, economic, and technology, energy becomes a crucial issue around the globe. A global warming devastation occurs from time to time and is becoming severe in the 21st century. Abrupt climate change happens around the world. Intergovernmental Panel on Climate Change (IPCC) is the responsible body to control the global temperature variation; it had announced that the global temperature absolutely increased with the estimation of 0.4 and 0.8°C for the past century and this phenomenon was the 10 warmest years over the last 15 years [1]. In the North Atlantic, the atmospheric circulation above Greenland also changed abruptly due to the global warming [2, 3]. Global warming phenomenon occurred as a result of greenhouse effect which led to the increasing in atmospheric temperature [3]. Increases in concentration of greenhouse gases such as nitrous oxide (N₂O), methane (CH₄), and carbon dioxide (CO₂) were the main causes of the drought in the areas from East Africa coastal area to the Arabian Sea, South Asia, East Asia, and South China. In the case of water (sea/river) level rising during the 21st century, global warming resulted in the melting of remaining ice masses. IPCC forecasts global mean sea levels (GMSLs) are likely to increase with the variation of 4-5 mm/year by 2050, 0.5–0.9 m by 2100, thus the losses of up to 30% of coastal wetlands [4]. Two major net heat sources had documented (1) net heating generated by human activities and (2) geothermal heat flow. In addition, the exploitation of nuclear energy and nonrenewable energy thus produces an additional heat in the world [5]. These driving forces lead the researchers to reduce the greenhouse effect and environmental protection with presenting creative ideas. In this paper, we are focusing on the alternative energy, hydrogen gas production. Today's hydrogen production is produced from fossil fuels, methane, and coal gasification [6]. The production of hydrogen gas determines the environmental impact and energy efficiency. Light-induced water splitting system is attractive to be studied. Thus, the photocatalysed degeneration of water with nanodisk-dendritic zinc oxide film was chosen to be the catalyst.

Zinc oxide is an n-type semiconductor, with direct wide band gap (3.37 eV) due to its electrons conductivity, and it has
Table 1: The different types of hexagonal ZnO disk based on preparation method.

<table>
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<tr>
<th>Researcher</th>
<th>Preparation methods</th>
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<tr>
<td>Yin et al. (2014)</td>
<td><em>Simple double-solvothermal method in the presence of glycine</em></td>
<td>Complex superstructure was assembled by hexagonal disks; the thickness of the disk is about 300 nm</td>
<td>[25]</td>
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<td>Zeng et al. (2009)</td>
<td><em>Hydrothermal method</em></td>
<td>Uniform single-crystalline ZnO nanodisks were well developed with 1.5 μm in diameter and 300 nm in thickness</td>
<td>[17]</td>
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<td>Zhang et al. (2007)</td>
<td><em>Electrodeposition method, HBO₃ as an electrolyte with zinc foil as anode, voltage 180 V, and the system kept at 2°C</em></td>
<td>Zinc/ZnO core-shell hexagonal nanodisk dendrites were produced with diameter from about 100 nm to several hundred nanometers and thicknesses are about 20–40 nm.</td>
<td>[15]</td>
</tr>
<tr>
<td>Li et al. (2007)</td>
<td><em>Electrochemical deposition method</em></td>
<td>The shape of the ZnO dendritic structure is similar to the branch of a fern; ZnO dendritic structure is in the range of 6–10 μm and 200 nm of thickness</td>
<td>[26]</td>
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<tr>
<td>Xu et al. (2004)</td>
<td><em>Vapour phase transport (VPT) method</em></td>
<td>Zinc oxide nanodisk; 3 μm in diagonal and 300 nm in thickness</td>
<td>[21]</td>
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the wurtzite hexagonal crystal structure. The stoichiometric excess of zinc ions is believed to cause the electrons conductivity where the zinc ions live in interstitial locations in the crystal lattice [7]. The other property of ZnO is the high exciton binding energy (60 meV) in ZnO crystal which can produce efficient excitonic emission under room temperature ultraviolet (UV) luminescence [8–10]. Moreover, rectification, optical properties, and chemical properties of ZnO bring great interest to the research world [9–16]. Synthesis method will determine the crystal shape from acicular needles to plate shaped crystal. By all means, this is the uniqueness of zinc oxide which can be made to form into a variety of crystalline shapes [17]. Furthermore, nearly neutral (pH ~ 6) system applied to the formation of ZnO nanostructures supports the environmental protection [17]. According to Table 1, electrochemical deposition method is likely to produce nanodisk-dendritic ZnO and disk-shape morphology is less familiar in research. At the same time, it has unique properties and leads to potential applications such as water-splitting process [18], electrodes for dye sensitized solar cells [19], and nanosensors [20, 21]. Equally important, the low active surface area and fast recombination losses of photoinduced charge carriers remain as a great challenge for ZnO nanostructures. Therefore, in this paper, the formation of nanodisk-dendritic zinc oxide was studied. The ability of nanodisk-dendritic ZnO photoelectrode in current-voltage characteristics and methyl orange (MO) degradation also has been studied.

2. Experimental Section

2.1. Synthesis of Nanodisk-Dendritic ZnO. ZnO nanostructures films were produced by electrodeposition process of zinc (Zn) foil (thickness 0.25 mm, 99.9% trace metals basis, Sigma-Aldrich) in a bath with electrolytes composed of 50 mL of 0.5 mM zinc chloride (ZnCl₂) and 50 mL of 0.1 M potassium chloride (KCl) at 3.0 V at temperature of 80°C. From our literature studies, 3.0 V and 80°C were selected in our study because the polycrystalline structure of ZnO will start to evolve at this potential difference and temperature with obviously and randomly oriented grains. The as-prepared pH of electrolyte is about 5–6, which was measured using a pH meter Mettler Toledo InLab Expert Pro. The electrodeposition process was conducted with two-electrode configuration system, where platinum electrode served as anode and Zn foil served as cathode. This closed system was then connected to a DC power supply. After electrodeposition process, the nanodeposit has been rinsed thoroughly with acetone for analysis Emsure Acs, Iso, Reag. Ph Eur for analysis and dried at atmosphere. The deposited ZnO nanostructured film was then annealed at 600°C for 3 hours because the zinc peaks will be negligible and completely oxidised [15].

2.2. Characterizations of Nanodisk-Dendritic ZnO. The crystallinity and phase transition of the samples were analyzed by using Bruker D8 Advance equipped with EVA-Diffract Software (Germany) X-ray Diffraction (XRD) with Cu Kα radiation and wavelength λ = 1.5418 Å. Meanwhile, the surface and cross-sectional morphologies of the samples have been viewed by Field Emission Scanning Electron Microscopy (FESEM) Quanta FEG 450 and the elemental analysis of ZnO nanostructured film was determined with Hitachi Energy Dispersive X-Ray Spectroscopy (EDX) analysis.

To study the photocurrent density of the sample, a three-electrode PEC cell with nanodisk-dendritic ZnO film served as anode, a platinum rod as the cathode, and a saturated calomel electrode (SCE) as the reference electrode arranged in a quartz cell filled with 1 M sodium hydroxide (NaOH) containing 1 v% of ethylene glycol. A 150 W xenon lamp (Zolix
Vis Spectrophotometer (UV-3101PC Shimadzu) was used to analyze the degradation percentage of MO solution. 

A UV-C Germicidal light. After leaving it in a reactor for 30 minutes in dark environment, 5 mL solution was withdrawn for every 1 hour from the quartz tubes to study the degradation of methyl orange (MO) solution after UV irradiation. Samples were photoilluminated at room temperature by using TUV 18W glass tube and placed in the photoreactor. The samples were analyzed at the ZnO phase. The Bragg reflection of ZnO phase was obtained after calcination process. All peaks were shifted to the left as the ZnO crystals were well and denser after calcination process. In addition, the nanodisk-dendritic ZnO sample is matched with the chemical formula ZnO (referring to XRD test) and consists of hexagonal crystal system. Besides, it also matched the wurtzite type because $a = 3.2498 \text{ Å}$, $b = 3.2498 \text{ Å}$, and $c = 5.2066 \text{ Å}$. The wurtzite type is important in semiconductor application as compared to other crystal structures of ZnO; zinc blende and rocksalt. The significance of wurtzite type ZnO was obtained from the ideal arrangement, by changing the $c/a$ ratio or the $u$ value. From experimental observation, $c/a$ ratios are smaller than ideal ones. In addition, $c/a$ ratio also showed the association of difference for two constituents' electronegativity. Consequently, components with the greatest difference show largest departure from the ideal $c/a$ ratio [22–24].

3.2. Morphological Structure of Nanodisk-Dendritic ZnO.

Substrate was shrill of nanodisk-dendritic ZnO (Figure 2(a)). The nanodisk-dendritic zinc oxides have a perfect hexagonal shape with diagonal of approximately 1.7 μm and thickness of approximately 150.4 nm. This result is in line with past researches at which nanodisk-dendritic ZnO exhibits unique characteristics and consists of overlapping nanodisks and self-tiered structure [15]. The stem and the leaflets were built of hexagonal nanodisks where they were self-arranged and self-assembled and became little leaves. The EDX spectroscopy analysis was performed and it showed average atomic percentage of 42.59% and 57.41% of zinc and oxygen, respectively, for as-prepared ZnO (Table 2). In this study, two-step process took place under dynamic electrolyte for the formation of nanodisk-dendritic ZnO. The first step was the formation of zinc hydroxide ($Zn(OH)_2$), followed by formation of zinc oxide (ZnO). However, this process occurred at all time until the reaction stopped. In the first place, the process started with dissolution of zinc chloride, potassium chloride and water to potassium ion ($K^+$), zinc ion ($Zn^{2+}$), chloride ion ($Cl^-$), and hydroxide ion ($OH^-$) and formation of hydrogen gas ($H_2$) occurred in the electrolyte by electrochemical process with energy supplied from direct electric current that separated the electrolyte into ions [27, 28] (1). Second, for the formation of zinc hydroxide ($Zn(OH)_2$) (intermediate growth stage), the $K^+$ (as directing agent) attracted the $OH^-$ to the cathode and produced increases in local pH, and saturation level changed at the cathode. When a supersaturation condition is reached, the nucleation of $Zn(OH)_2$ precipitation...
occurred on the substrate surface (cathode) (2). The formation of zinc oxide (ZnO) occurred by dehydration process of Zn(OH)$_2$ on the substrate (3). At the beginning of deposition process, the Zn$^{2+}$ concentration at the substrate surface decreased when pH is increased leading to slowest growth rate towards (0001). Diffusion of Zn$^{2+}$ from (0001) to the substrate surface leads to the unit growing at preferential growth of [1000] direction. When many nanodisks stacked together, it is important to realize that their arrangements on the substrate were on horizontal position (1000) which is in the x-axis direction and it is clearly seen in symmetry shape. The crystal growth velocity along various planes depended on the atomic packing density [15].

Below are the equations related to the formation of ZnO:

Dissolution of KCl + ZnCl$_2$ + H$_2$O is as follows:

\[
\text{KCl} \rightarrow \text{K}^+ \text{(aq)} + \text{Cl}^- \text{(aq)}
\]

\[
\text{ZnCl}_2 \rightarrow \text{Zn}^{2+} \text{(aq)} + 2\text{Cl}^- \text{(aq)}
\]

\[
2\text{H}_2\text{O} \rightarrow \text{H}_2 \uparrow + 2\text{OH}^- \text{(aq)}
\]

Formation of zinc hydroxide (Zn(OH)$_2$), KOH, and KCl is as follows:

\[
\text{K}^+ \text{(aq)} + \text{OH}^- \text{(aq)} \rightarrow \text{KOH}
\]

\[
\text{Zn}^{2+} \text{(aq)} + 2\text{OH}^- \text{(aq)} \rightarrow \text{Zn} \text{(OH)}_2
\]

\[
\text{H}_2 \uparrow + 2\text{Cl}^- \rightarrow 2\text{HCl}
\]

Formation of zinc oxide (ZnO) is as follows:

\[
\text{Zn} \text{(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \text{ (dehydration process)}
\]

\[
\text{HCl} + \text{KOH} \rightarrow \text{H}_2\text{O} + \text{KCl}
\]

Past researches found the formation of dendrite shape due to the fast growth velocity of Zn ion in the electrolyte [29, 30]. Growth mechanism occurred in global diffusion and later oriented attachments were localized. Dislocation from the early crystal growth happened due to the high velocity of electrolyte (>350 rpm). Therefore, the second hexagonal nanodisk has grown slightly dislocated from the earlier crystal. Another key point is that nanodisk-dendritic tips were known to grow in the direction of maximum surface energy. The (1000) facet was out of sorts; therefore it contributed to highest effective surface energy [15, 31].

3.3. Photocatalytic Activity Evaluation. The photocatalytic activities of the nanodisk-dendritic ZnO and as-prepared ZnO were investigated using the MO degradation method under UV light radiation with the purpose to support the photocatalytic activity argument of nanodisk-dendritic ZnO. It was confirmed that nanodisk-dendritic ZnO exhibited good photocatalytic property when MO solution was degraded for approximately 80% after 6 hours under UV irradiation. Nanodisk-dendritic ZnO exhibited higher photocatalytic activity compared to as-prepared ZnO with MO concentration 18% after 6 hours (Figure 3(a)). Decomposition of MO solution can be explained by an oxidation process that took place on the surface of nanodisk-dendritic ZnO via photogenerated hole. In other words, an electron-hole pair existed in the absence of light intensity [32–34]. Under UV light illumination, energy produced was higher than nanodisk-dendritic ZnO band gap energy. Therefore, electrons at the conduction band and holes at the valence band were generated. Holes at the nanodisk-dendritic ZnO surfaces react with water to form highly reactive hydroxyl radicals (OH$^\cdot$), and at the same time oxygen acts as an electron acceptor by being a superoxide radical anion [35]. The superoxide radical anions from hydroxyl radicals have an excellent oxidation ability [36] which may degrade organic dye, and, in MO decomposition, it was degraded to carbon dioxide and water [31]. Nanodisk-dendritic ZnO showed high photocatalytic property due to its high surface area and active photoresponse (2D structure).
Figure 3: Photodegradation of MO solution by (a) nanodisk-dendritic ZnO and (b) as-prepared ZnO with increasing degradation time.

Figure 4: Current density-voltage characteristics for (a) nanodisk-dendritic ZnO and (b) as-prepared ZnO under ultraviolet ray and (c) nanodisk-dendritic ZnO without illumination.

Figure 5: Current density-voltage characteristics for (a) nanodisk-dendritic ZnO, (b) as-prepared ZnO under visible light, and (c) nanodisk-dendritic ZnO without illumination.

3.4. Photoelectrochemical Response. A scanning potentiostat by mean to measure current (I) under an applied potential (V) could test the efficiency of nanodisk-dendritic ZnO photocatalytic activity. For water electrolysis application, the efficiencies of over 90% are at −1 to 1 V [37, 38]. From now on, in order to understand the efficiency nanodisk-dendritic ZnO thin films in water electrolysis, sample was evaluated and tested their I-V characteristics between −1V and 1V. Figure 4 was plotted to exhibit I-V characteristic curves for the (a) nanodisk-dendritic ZnO, (b) as-prepared ZnO under ultraviolet ray, and (c) nanodisk-dendritic ZnO without illumination. The significant photocurrent density $j_p$ of an average value of 19.87 mA/cm$^2$ for nanodisk-dendritic ZnO under ultraviolet ray (Figure 4(a)) was obtained as compared to 6.43 mA/cm$^2$ for as-prepared ZnO under ultraviolet ray (Figure 4(b)) and 1.49 mA/cm$^2$ for nanodisk-dendritic ZnO without illumination (Figure 4(c)). The catalytic activity contribution can be observed from photocurrent density differences under ultraviolet ray illumination and without ultraviolet ray illumination. However, the current density $j$ value decreased with the increasing of spectrum wavelength until visible light spectrum (390–700 nm) is reached. Under visible light, average $j_p$ of 14.05 mA/cm$^2$ was observed for the nanodisk-dendritic ZnO (Figure 5(a)), which is relatively higher when compared to as-prepared ZnO under visible light: $j_p$ 2.14 mA/cm$^2$ (Figure 5(b)) and nanodisk-dendritic ZnO without illumination: 1.49 mA/cm$^2$ (Figure 5(c)).

Based on the results of $j$-V characteristic curves (Figures 4 and 5), as-prepared-ZnO film showed poor result due to the existence of oxygen vacancies inside the ZnO bulk, which points to the increasing number of recombination centers. The recombination centers clearly contributed to the decreasing of photoinduced $e^-\overline{}$ mobility and back to the contact of Zn substrate because of series of resistance caused by increasing trap states. Besides, the amorphous phase comprises high concentration of other material defects such as impurities, dangling bonds, and microvoids, which similarly act as recombination center and result in a decrease of $j_p$ [39]. Predominantly, as-prepared-ZnO film is basically unable to develop a regular depletion region [40]. It was found that the $j_p$ of heat treated (600°C) nanodisk-dendritic ZnO sample was slightly increased to 19.87 mA/cm$^2$, which suggests that crystal structure of nanodisk-dendritic ZnO sample can improve the photocurrent generation effectively. In addition, the high specific surface area of nanodisk-dendritic architecture might have contributed to the strong light scattering effects and incident light absorption from any direction. In the electrolyte, the large active surface area established the photoinduced electrons and these electrons transferred to the substrate. By the use of external circuit, the photoinduced electron travels to counter electrode (platinum electrode) and enhances the photocatalytic activity and photoelectrochemical response significantly.
4. Conclusions

In this paper, nanodisk-dendritic ZnO with perfect hexagonal shape was fabricated by a simple one-step electrodeposition process with 600°C calcination temperature. From the characterization methods, it indicates that the sample is nanodisk-dendritic zinc oxide; with chemical formula, ZnO, and consists of hexagonal crystal system. It lies under tetragonal wurtzite type because $a = 3.2498 \text{ Å}$, $b = 3.2498 \text{ Å}$, and $c = 5.2066 \text{ Å}$. The photocatalytic test (photocurrent density and methyl orange degradation) confirmed that nanodisk-dendritic zinc oxide has excellent photocatalytic activity. Prolonged electrodeposition time or increase of the ZnCl$_2$ concentration may increase the volume of nanodisk-dendritic ZnO and produce better photocatalytic activity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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