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Construction of ZnO-Nanoflowers Photoanode for Photoelectrochemical Cell

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Abstract. ZnO-nanoflowers on a transparent conductive tin-doped In₂O₃ (ITO) glass substrate have been successfully prepared via a simple and efficient growth approach that is combining of dip coating and hydrothermal processes. One thin layer of ZnO nanoparticles is prepared by dip coating method followed by hydrothermally grown of ZnO nanoflowers at low temperature. The morphology and structure of ZnO-nanoflowers were inspected by field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD), respectively. The optical absorption and photoluminescence spectra of ZnO-nanoflowers are also investigated. The ZnO-nanoflowers photoanode shows dramatically contributed to the separation of electron-hole pairs and enhanced the photoreponse. The photocurrent density is 0.44 mA/cm² indicated that the PEC cells based on ZnO-nanoflowers photoanode have promising application potential in overall solar energy.

1. Introduction
Recent advances in nanotechnology focused on nanomaterials have been subject to intensive studies as a vital category of materials. Wide bandgap-semiconductor materials, such as ZnO and TiO₂, have more investigated due to their significance in potential applications. The widely-studied and one of the most crucial materials in the fields of nanotechnology is Zinc oxide (ZnO). A semiconductor ZnO (n-type) is one of the compounds II-VI semiconductors with a large exciton binding energy of 60 m eV, a energy-gap 3.37 eV [1], and a hexagonal wurtzite structure. Furthermore, the preparation method is an effective key to construction various forms of nanostructures with diverse properties [2]. Whereas the nanomaterials with various electrical and optical properties are determined via the shape and size of the particles, thus the fabricated synthesis of the particles is the crucial factor for nanostructured material. Various nanostructures of ZnO compound for instance nanoparticles, nanorods, nanowires, nanoflowers and, nanotubes have investigated in numerous applications.

Up to now, much effort of scientific research has been done based on nanostructured ZnO nanorods for photoelectrochemical cells due to its potential applications in storage energy [3]. However,
nanostructured ZnO nanoflowers thin films are presently lower investigation for photoelectrochemical applications. This study focused on ZnO nanoflowers nanostructure which found widely applications in solar cells [4], photodiode [5], photodetectors [6] and sensors [7]. For the synthesis of ZnO nanoflowers, they have utilized a diversity of procedures, like high-temperature vapor-liquid-solid or thermal evaporation processes. Additionally, in those techniques, some catalysts such as gold nanoparticles and a high vacuum with temperature have required.

Presently, the methodologies of aqueous solution synthesis constructed on wet chemical processes have much published. To prepare ZnO nanostructures, there are various deposition techniques that have been utilized to deposit non-doped and doped ZnO thin films like chemical vapor deposition (CVD), magnetron sputtering deposition (MSD), pulsed laser deposition (PLD), sol-gel process and spray pyrolysis (SP) [8–12]. Thus, the doping approaches for thin films are more quite employed to improve the electrical and optical properties of semiconductors [13]. The current work is focused on the synthesis and investigation of the growth of ZnO-nanoflowers for the photoelectrochemical application by the simple hydrothermally system via a chemical method.

2. Experimental

2.1. Preparation of ZnO Nanoflowers

ZnO nanoflowers were grown on indium-doped tin oxide (ITO) glass substrate which was used as substrate via two facile methods. Prior to that, the ITO glass substrate was ultrasonically washed in a sequential manner for 15 mins each in acetone, 2-propanol, and deionized water then dried in the air at room temperature. In the first step, the ZnO seed layer was prepared by the dip-coating method. Where it is prepared by dissolving 0.1 M of zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O) in a mixture of equal volume (10 mL) of deionized water and ethanol. The solution was stirred for a half hour at 60 °C. The ITO glass substrate was dipped in the ready solution for one minute followed that heating at 100 °C for 15 mins and repeated this step for three times. It was then annealed at 300 °C for one hour with a heating rate of 2 °C/min. In a secondly way, a hydrothermal method at low temperature is used to prepare ZnO nanoflowers. Where it is prepared by dissolving 0.05 M zinc nitrate (Zn(NO$_3$)$_2$·6H$_2$O) in 50 mL deionized water and 0.5 M hexamethylenetetramine (CH$_2$)$_6$N$_4$) in 100 mL deionized water. The mixture solution was stirred for two hours. The coated substrate of the seed layer was vertically dipped in the mixture solution for four hours at an oven temperature of 85±5 °C. After finishing the growth period, the substrates were removed from the solution and were thoroughly washed with deionized water to eliminate the residual materials from the surface of the film. Lastly, a prepared film was annealed at 450 °C for one hour and this resulted in the formation of ZnO nanoflowers.

2.2. Characterizations of ZnO Nanoflowers

The field emission scanning electron microscopy (FESEM, JOEL JSM-7600F, Japan) was used to inspect the surface morphology of the prepared ZnO nanoflowers. The structure and phases of the samples were analyzed by X-ray diffractometry (Panalytical X’Pert Pro MPD diffractometer) by using CuKα radiation (λ = 1.54 Å) at 40 kV and 40 mA. Absorbance spectra of the prepared sample were measured using Lambda 20 Ultraviolet-visible spectrophotometer (Perkin Elmer Instruments). The PL emission spectra were obtained using a Perkin–Elmer LS-55 spectrophotometer.

2.3. The photoelectrochemical response of ZnO Nanoflowers

The sample of ZnO nanoflowers was used as working electrode, Ag/AgCl as the reference electrode and Pt wire as the counter electrode in a conventional three electrode cell system, as shown in Figure 1. The photoelectrochemical measurement was carried out using linear sweep voltammetry (Autolab PGSTAT204/FRA32M module) to control the potential and record the corresponding photocurrent at the scan rate of 20 mV s$^{-1}$ in a mixture of 0.1 M Na$_2$S and 0.1 M Na$_2$SO$_3$ electrolyte (pH = 13) under illumination 100 mW cm$^{-2}$. 
3. Results and discussion
The FE-SEM images of the prepared ZnO nanoflowers with a varied-magnification show in Figure 2. It is revealed that ZnO morphology resembles a flower bunch synthesis of ZnO-nanoleaves. The bunch of nanoleaves which grown approximately from same seed formed like nanoflowers can be seen clearly. These ZnO nanoleaves have a regular length (1.1 μm) with a diameter of 100±30 nm since the diameter growth rate of leaves start wide then decrease upwards. The ZnO nanoleaves were grown and penetrate through a thin layer of ZnO NPs which its thickness around ~ 40 nm. As declared in the study of Greene et al. [14], it is desirable for electronic applications to make the nanoparticle layer as thin and continuous as possible to enhance the well-oriented of ZnO that are mostly in close contact with the substrate.
Figure 2. Field emission scanning electron microscopic images of the ZnO nanoflowers at different magnifications.

Figure 3 shows the XRD pattern of ITO glass and ZnO nanoflowers. All the peaks match well with the ITO glass indexed as cubic (JCPDS card no. 039-1058) or to bulk ZnO, which could be indexed as the hexagonal wurtzite structure of ZnO (a=b=3.2489 Å, c = 5.2062 Å, JCPDS card no. 003-0888). Furthermore, it can be seen that the (100) and (002) diffraction peaks are lower compared to the (101) direction. Table (1) illustrates the results of XRD analysis for the ZnO nanoflowers synthesis in this search. The crystallite size by Scherrer’s relation was 20.5 nm which could be smaller than the reported value of ZnO nanoflowers [15]. Moreover, the lattice parameters were found to be a=b=3.0037 Å and c=5.1936 Å. No appearances peaks of other impurities were distinguished in XRD pattern, showing that phase-pure and high-quality ZnO nanomaterials are readily obtained.
Table 1. XRD analysis for ZnO nanoflowers.

| hkl  | (100) | (002) | (101) |
|------|-------|-------|-------|
| 2θ (deg.) | 31.847 | 34.511 | 36.287 |
| d-spacing (nm) | 2.8077 | 2.5968 | 2.4737 |
| FWHM (deg.) | 0.3840 | 0.3840 | 0.4080 |

Figure 3. XRD patterns (a) ITO glass and (b) ZnO nanoflowers.

The optical absorption spectra of ZnO nanoflowers is showed in Figure 4. The fact is ZnO has a direct bandgap which has confirmed via the absorption edge which is located at 378 nm. To locate the type and value of the optical band gap can be utilized an essential absorption, which counterpart the excitation of an electron from the valence level to the conduction level. As shown in the inset of Figure 4, by extrapolating the linear portion of the curve to meet the hυ axis the band gap values can be determined. After band gap calculation, it is found to be 3.28 eV.
Figure 4. UV-VIS optical absorption spectrum of ZnO nanoflowers.

Figure 5 shows the separately PL emission spectra shown two diverse emissions. Firstly, the near-band-edge (NBE) emission is around 383 nm in the region of UV, was created from the transition of a photo-generated electron from the conduction level to the valence level due to recombination of free excitons. Secondly, the deep-level –emission (DLE) in the region of the visible around (450–800) nm was created to the transition of an electron from the conduction level to the defect state level (such as V_{Zn}, Zn_{i}, V_{o}, and O) then to the valence band [16]. It can clearly observe UV emission centered at 383 nm (3.23 eV) arising from e–h recombination across the conduction band (CB) and valence band (VB) of ZnO nanoflowers. Moreover, the PL peak at around 456 nm mainly results from oxygen vacancies (V_{o}). It can also be noted that the peaks at 529 nm and 626 nm are generated by the conduction band to interstitial oxygen transition (O_{i}). The peak positions are also consistent with previous reports [17,18].
Figure 5. Room temperature PL spectrum of ZnO nanoflowers.

In the photo-illumination process, light is illuminated on the surface of ZnO nanoflowers and holes with electrons are generated. \( \text{Na}_2\text{S} \) and \( \text{Na}_2\text{SO}_3 \) aqueous solution acts as the hole scavenger. The production of \( \text{S}_2^{2-} \) ions serving as an optical filter and compete with reduction of protons and efficiently suppressed by mixing with \( \text{SO}_3^{2-} \) ions. \( \text{SO}_3^{2-} \) ions yield mainly thiosulfate ions. Finally, the mechanism to generate photocurrent occurred in the aqueous \( \text{S}_2^{2-} + \text{SO}_3^{2-} \) solutions:

\[
\text{SC (n-type)} + \text{hv} \rightarrow \text{SC (n-type)} \left[ e^{-}_{\text{C.B.}} + h^{+}_{\text{V.B.}} \right] \tag{1}
\]

The electrons in semiconductor SC (n-type) are collected at the back contact (ITO). Then, counter electrode allocated them to harvest an anodic photocurrent. The holes are preferentially scavenged by sacrificial reagents \( \text{SO}_3^{2-} \) and \( \text{S}^2 \) under visible light illumination. The reactions occurred at photoanode (working electrode) are [19]:

\[
\begin{align*}
\text{S}^2 + 2h^{+}_{\text{VB}} & \rightarrow \text{S}_2^{2-} \tag{2} \\
\text{S}_2^{2-} + \text{SO}_3^{2-} & \rightarrow \text{S}_2\text{O}_3^{2-} + \text{S}^2 \tag{3} \\
\text{SO}_3^{2-} + \text{S}^2 + 2h^{+}_{\text{VB}} & \rightarrow \text{S}_2\text{O}_3^{2-} \tag{4} \\
\text{S}_2\text{O}_3^{2-} + \text{H}^+ & \rightarrow \text{H} \text{SO}_3^- + \text{S} \tag{5}
\end{align*}
\]
The reaction occurring at the counter electrode is:

\[ S + 2e^- \rightarrow S^2^- \]  \hspace{1cm} (6)

Figure 6 displays the photocurrent density of photoanode (sample) in a three-electrodes system with an aqueous electrolyte of 0.1 M Na₂SO₃ and 0.1 M Na₂S. The scanning range was around (1.0 V to -1.0 V) versus the reference electrode Ag/AgCl. Here, ZnO nanoflowers coating showed the maximum photocurrent density of 0.44 mA cm⁻² under an illumination intensity of 100 mW/cm², which is higher than the already reported value for ZnO nanoflowers at the applied potential of 0.6 V versus Ag/AgCl [20]. The equation of the photoconversion efficiency as a function of applied potential vs. Ag/AgCl is \[ \eta = I_{ph} \left(1.23 - V_{app}\right)/J_{light} \] [21,22], where \( V_{app} \) is the applied voltage in volt and \( I_{ph} \) is the photocurrent density in mA cm⁻². Whereby, \( J_{light} \) is the illuminated intensity of incident light in mW cm⁻² and in the same electrolyte system. Thus, the photoconversion efficiency value at 0 V was 0.54 % which is higher than the stated value for ZnO nanorods [23]. ZnO nanoflowers photoanode exhibited the photoresponse effect in the positive potentials under illumination. With the applied voltage (\( V_{app} \) vs. Ag/AgCl) becoming more positive, the photo-enhancement current density of the photoelectrode will be increased. Hence, the n-type conductivity of the sample in this study was investigated.

![Figure 6](image-url)
4. Conclusion
A simple technique to synthesis the ZnO nanoflowers in nanometer scales were obtainable to efficiently used in convert solar energy into electricity. ZnO nanoflowers with particular morphology were successfully prepared by treated of ZnO nanoparticles via the hydrothermal process. The photocurrent density of ZnO nanoflowers in a three-electrode system has exhibited around 0.44 mA cm$^{-2}$ under the illumination. Thus, these results might be potentially used in current application due to its simple preparation method with controlling nanoflowers growth.

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