

Comparison on Photo-Electro Chemical Properties of ZnO Electrode with Different Natural Dyes

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Abstract. Zinc oxide (ZnO) powder was firstly prepared by hydrothermal synthesis at low temperature (120 °C). UV-vis spectroscopic study was used to indicate different peaks for mixed colourants available in their extract in both UV and visible region. X-ray diffraction (XRD) investigation was carried out to examine the structural properties of ZnO powder. ZnO colloidal solution was deposited onto ITO/glass by rolling. After air dry, annealing in O₂, atmospheric ambient was performed at 300 °C and 400 °C for 1 h. As the surface treatment, sintered ZnO film was immersed in 0.1 M HCl, washed with DIW and dried at room temperature. The curcumin, yellow-orange dye, found in turmeric root and ginger (*Zingiber Officinale Roscoe*), brown, were used as the photosensitizer and they were carefully prepared to avoid colour fading. After that, the ZnO films were immersed in dye solutions for 24 h. High performance carbon counter electrode was prepared and used as a counter electrode. Two glass slides were offset and two binder clips were used to hold the electrodes together. Photovoltaic responses of ZnO cells were measured and they were expected to utilize the DSSC application. The conversion efficiency of DSSC with curcumin dye gave 0.13% at 400 °C and at 0.12% at 300 °C whereas the conversion efficiency of DSSC with ginger dye resulted 2.02% at 400 °C and 2.88% at 300 °C.

Keywords: Hydrothermal synthesis, ITO/glass, Curcumin, Ginger, DSSC.

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INTRODUCTION

Hydrothermal technique is a promising alternative synthetic method because of the low process temperature and very easy to control the particle size. The hydrothermal process have several advantage over other growth processes such as use of simple equipment, catalyst-free growth, low cost, large area uniform production, environmental friendliness and less hazardous. This method has been successfully employed to prepare nanoscale ZnO and other luminescent materials [1, 2]. Zinc oxide (ZnO) is one of the important prospective short wavelength emitters owing to its large excitation binding energy and a wide energy gap of 3.3 eV at room temperature [3]. Zinc oxide is widely used in various applications such as photonic devices [4], solar cell windows, plasma display panels [5], surface acoustic wave devices [6], gas sensors [7], luminescent materials, transparent conductor, heat mirrors and coatings [8]. The dye-sensitized solar cells (DSSC) differ from the conventional solid-state devices in the way they process the photon-to-electric conversion [9]. ZnO films composed of nanoparticles are sensitized with natural derived dyes to achieve higher photo-conversion efficiencies [10]. Dye-sensitized solar cells (DSSCs) were low cost and can be easily prepared. In

order to improve conversion efficiency of dye-sensitized solar cells, the sensitizer should be panchromatic, that can absorb photons over the entire visible region of the solar spectrum while maintaining sufficient thermodynamic driving force for both the electron injection and dye generation process [11]. Curcumin is well-known for its pharmaceutical applications had not gained much insight as a photosensitizer, in spite of its photoactivity in the visible region of the solar spectrum [12]. Curcumin-derived from *Curcuma longa* rhizomes (turmeric), has high thermal and chemical stability, eco-friendly, along with low production cost that would be certainly interesting as a natural derived dye sensitizer in DSSCs applications. The chelating behavior of Curcumin dye is well-matching to ZnO (Zn²⁺) rather than TiO₂ (Ti⁴⁺) [13]. The Curcumin dye in the DSSC and TiO₂ electrode has been reported by Sreekala C O et al [14]. The ZnO films composed of nanoparticles are sensitized with natural derived dyes to achieve higher photo-conversion efficiencies. The electronic band structures of these Curcumin-derived dyes facilitate in excitation-splitting and electron-transfer from the dye singlet state to the ZnO conduction band [15]. Ganesh T et al (2010) reported that the fill factor and efficiency of ZnO electrode sensitized Curcumin-derived dyes were 0.45 and 0.34% [10]. Ginger (*Zingiber Officinale Roscoe*; family Zingiberaceae)

[16] is a mono-cotyledonous, sterile cultigen thought to have originated in India or Southeast Asia, from where it was introduced to other parts of the world [17]. The important active component of ginger root is the volatile oil and pungent phenol compound such as gingerol, which is a very potent anti-inflammatory compound [18]. In this paper, photo-electro chemical properties of ZnO electrode DSSCs at curcumin dye and ginger dye were compared.

EXPERIMENTAL DETAILS

Materials and Methods

Making Window for DSSC Photo-Electrodes

Firstly, eight indium-tin-oxide (ITO) coated glass substrates were cut into 1.5 cm × 1.5 cm pieces to observe four pairs of DSSCs; two pairs with curcumin dye at 300 °C and 400 °C annealing temperature and two pairs with ginger dye at those temperatures. And then, these substrates were rinsed with acetone, methanol and deionized water step by step. After air drying, masking tapes were adhered along the peripheral of ITO coated glass substrates. Thus, only the central area of 0.5 cm × 0.5 cm was reserved for the DSSC photo-electrodes.

Hydrothermal Synthesis of ZnO

In this work, ZnO powder prepared by a simple hydrothermal process was used to fabricate the working electrodes (photo-anodes) for DSSC applications. The raw materials of zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH) and methanol (CH_3OH) were chosen as starting chemicals. In order to synthesize the ZnO fine powder, the solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.1 M) was prepared in 50 ml methanol under stirring. NaOH (0.4 M) solution prepared in 25 ml methanol was added to this sol under continuous stirring. These solutions were transferred into Teflon lined sealed stainless steel vessel. Then this mixture solution was heated at 120 °C for 6 h. It was then allowed to cool at room temperature. Finally, ZnO fine powder was formed.

ZnO Layer Preparation

Hydrothermal synthesized ZnO powder was dissolved in 2-methoxyethanol and refluxed with oil bath to form transparent and colloidal solution. During the preparation detergent was added into it as a surfactant. It was coated onto clean ITO/glass substrates for four pairs of ZnO DSSCs by rolling

method. After air drying, two substrates were annealed at 300 °C and next two substrates were annealed at 400 °C for 1 h. Those substrates were immersed in 0.1 M HCl for 1 h and washed with DIW maintained 1 h for surface treatment. Thus ZnO films (active area = 0.5cm × 0.5cm) were formed on ITO/glass substrates.

Dye Extraction

Curcumin and Ginger Powder Preparation

First of all, turmeric root (Curcumin) was cured in boiled water for 45 min to be softer and enhanced colour. The outside layer of turmeric skin was peeled off and sliced it into some pieces. It was naturally dried for a week (7 days) to avoid colour fading. After air drying, it was ground into a fine curcumin powder. Similarly, ginger powder was prepared from ginger root (*Zingier Officinale Roscoe*; family *Zingiberaceae*). Figure 1 showed the turmeric root (Curcumin) and the ginger root (*Zingier Officinale Roscoe*) was shown in Figure 2.



FIGURE 1. Turmeric root (Curcumin)



FIGURE 2. Ginger (*Zingiber officinal Roscoe*)

High Performance Curcumin and Ginger Dye Extraction

The curcumin powder was packed with thin cloth and cured in acetone and the acetone changed its colour into yellow-orange. Some powder was acidified with 1% H_2SO_4 , mixed with acetone and annealed at 80 °C for 30 min. The solutions obtained from two different methods were mixed and the pH reached 6. In the same way, ginger dye was observed. In this point the pH value of ginger dye was 5. The KOH base

was added to get the neutral curcumin dye (yellow-orange) and ginger dye (brown) solution.

DSSC Fabrication

Dye-Sensitized ZnO Photoanode Preparation

Two substrates of ZnO sintered at 300°C and 400°C were soaked in extracted curcumin dye solution for 24 h, and other two substrates of ZnO sintered at those degrees of temperature were also soaked in extracted ginger dye solution for 24 h so that dyes can be fully absorbed by ZnO. After that these were washed in H₂O and ethanol step by step. Then ZnO photoanodes at different natural dyes were obtained by drying at 100°C for 1 h.

Carbon Counter Electrode Preparation

The last four ITO coated glasses were prepared into carbon counter electrodes to prevent passing through the light from the anode of DSSCs. The black carbon (0.4 g) was dispersed into the mixture solution of water (16 ml) and ethanol (8ml). After dispersion, carboxyl-methylcellulose (0.24 g) was also added and adhesive carbon paste was formed. It was coated onto ITO/glass substrates and annealed at 180 °C for 1 h.

DSSCs Architecture

ZnO photoanodes were assembled with carbon counter electrodes by two binder clips. Iodine was injected and it was used as a mediator to form the DSSCs. Finally, two pairs of DSSCs with curcumin dye at 300 °C and 400 °C and two pairs of DSSCs with ginger dye at these degrees of temperatures.

RESULTS AND DISCUSSION

XRD Analysis

Figure 3 showed the XRD profile of ZnO sample at 0.4 M. The sample was prepared at temperature 120°C for 6 h. Specimen was scanned from 10° to 70° in diffraction angle, 2θ with step-size of 0.02°. The standard or reference profile was # 75-0576 > ZnO JCPDS library file. On this XRD spectrum, nine peaks were well-consistent with the ZnO JCPDS library file. They were (100), (002), (101), (102), (110), (103), (200), (112) and (201) respectively. The XRD diffraction peaks belonging to (100), (002) and (101) planes of ZnO hexagonal phase were observed in the XRD spectrum. The intensity of (002) diffraction was the weakest among them. The most intense peak was

caused by the (101) reflection. The dominant peak was also (101) reflection. In addition, some extra peaks were formed on XRD spectrum and they were unidentified. The crystallite size was determined to be 21.5 nm.

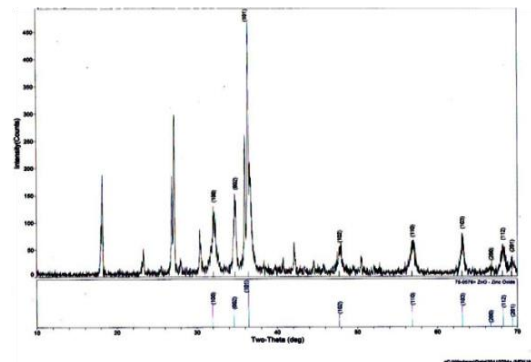


FIGURE 3. XRD Spectrum of ZnO Powder

UV-vis spectroscopic study

UV vis spectra of any colourant/dye show its peaks at predominating wavelength, indicating main hue. For natural dyes, the spectra specially indicated different peaks for mixed colourants available in their extract in both UV and visible region. This analysis was carried out using UV-1800 SHIMADZU UV spectrophotometer with the wavelength 190-1100 nm range. Figure 4 showed the UV-vis absorption measurement for ZnO. The UV-vis absorption measurement of curcumin dye was showed in Figure 5. Figure 6 indicated the UV-vis measurement of ginger dye. From the UV data analysis, ZnO showed one major absorption peak at 369 nm and the ginger dye did not show much difference from ZnO in the visible spectrum. Its maximum absorption peak was 363 nm by using acetone solvent. The absorption peaks of curcumin dye were 288 nm and 464 nm. Popoola et al [19] reported that the wavelength of maximum absorption of ginger rhizome dye is 420 nm in their study. From these results, we can conclude that the observed wavelength value of ginger dye was within the near ultraviolet region and the reference wavelength value was within the visible region. The wavelength values of curcumin dye are near ultraviolet region and also within visible region. The band gap values could be determined from the respective wavelength values. According to the band gap values, ginger dye was more acceptable with ZnO than curcumin dye. Table 1 showed the analysis datas of ZnO, curcumin and ginger dye by UV-Vis spectroscopy.

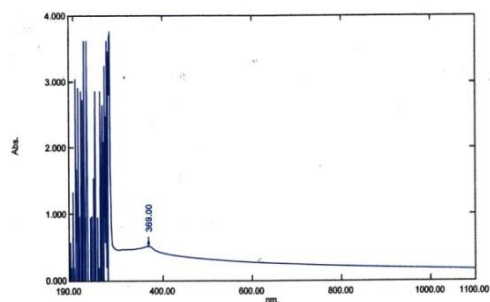


FIGURE 4. UV/Vis Absorption Measurements for ZnO

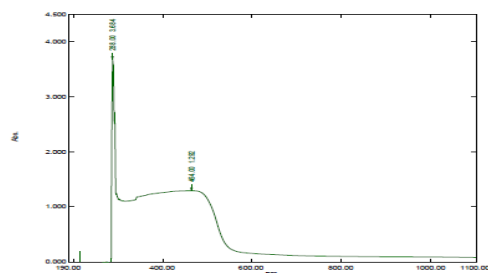


FIGURE 5. UV/Vis Absorption Measurements for Curcumin Dye

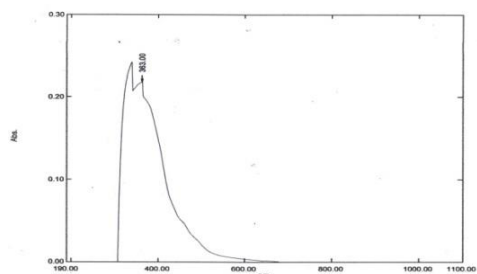


FIGURE 6. UV/Vis Absorption Measurements for Ginger Dye

TABLE 1. Analysis Data of ZnO, Curcumin and Ginger Dye by UV-Vis Spectroscopy

Sample	Wavelength (nm)	Abs.	Band gap (eV)
ZnO	369	0.51	3.19
Curcumin	288	3.68	1.65
Curcumin	464	1.29	1.65
Ginger dye	363	0.22	2.36

Photovoltaic Response

The J-V characteristics of ZnO-based curcumin derived DSSC was shown in Figure 7 and those of ZnO-based ginger derived DSSC were measured and shown in Figure 8. Effect of annealing temperature on photo-voltaic parameters of ZnO electrodes sensitized

with ginger dye were calculated and described in Table 2.

TABLE 2. Effect of Annealing Temperature on Photo-voltaic Parameters of ZnO Electrodes Sensitized with Curcumin Dye & Ginger Dye

Annealing Temperature (°C) & Sample	J_{sc} (mA/cm ²)	V_{oc} (mV)	P_m (mW/cm ²)	η (%)	Ff
300-Curcumin	1.66	118	0.116	0.12	0.59
400-Curcumin	1.74	124	0.129	0.13	0.60
300-Ginger	0.15	172	17.6	2.88	0.68
400-Ginger	0.16	111	12.3	2.02	0.72

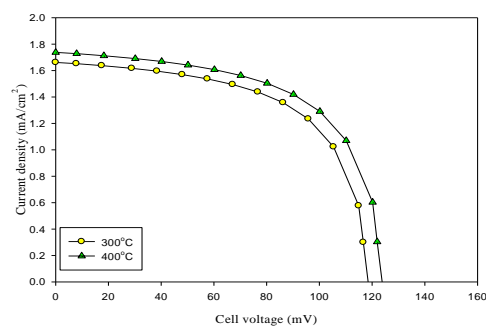


FIGURE 7. J-V Curves of ZnO Electrode with Curcumin Dye Sensitized Solar Cells at 300°C and 400°C

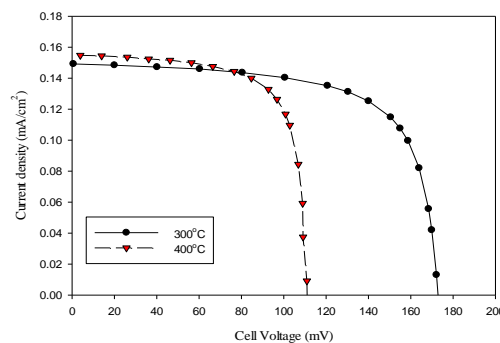


FIGURE 8. J-V Curves of ZnO Electrode with Ginger Dye Sensitized Solar Cells at 300°C and 400°C

CONCLUSION

In this study, we tried to improve the conversion efficiency of the DSSCs by using the different natural dyes. The purpose of this work is also to study the crystallographic structure of ZnO prepared by hydrothermal technique, predominating wavelengths of colourant/dye available in their extract in both UV and visible regions. From this research, like curcumin dye molecules, also ginger dye molecules can make

the electron transport very rapidly, and thus, which can be also used as the photosensitizer. Unlike the curcumin dye is that the wavelength of ginger dye is better matched with ZnO's than curcumin dye. The well matching of ZnO and ginger dye can offer larger specific surface areas for dye absorption, direct pathway for electron transport, and light-scattering effects that extend the travelling distance of light within the photoelectrode film. Hence, compared to two natural dye photosensitizers, ginger dyes have better absorption quality than curcumin dyes. The conversion efficiencies of ginger-based DSSCs at both temperatures are better than those of curcumin-based DSSCs. The conversion efficiencies of all DSSCs were observed to be the range (0.12% - 2.88%) and indicated the industrial requirements although the methods used to fabricate the DSSCs was non-expensive, non-modernized and non-complicated methods. Even between the ginger-based DSSCs at different temperatures (300 °C and 400 °C), the conversion efficiency of 2.88% at 300 °C is better. For summarized, several attempts to expand ZnO concepts to different natural dyes are presented to motivate further improvement in the conversion efficiency of DSSCs.

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