FULL PAPER

Synthesis of ZnO nanostructures by microwave irradiation for energy conversion material in for dye sensitized solar cells and materials for photocatalytic dye degradation applications

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ZnO nanoplates and ZnO nanostructure flowers were successfully synthesized in alkaline solutions containing different contents of sodium hydroxide by a cyclic-microwave method. The as-synthesized products were characterized by X-ray Diffraction, Field Emission Scanning Electron Microscopy and ultraviolet (UV)-visible spectroscopy. The crystal structure of ZnO nanoplates and nanostructure flowers are wurtzite structure with energy band gap of 3.201–3.217 eV. In this research, these products were applied as energy harvesting materials in dye sensitized solar cells (DSSCs) and also used photocatalytic degradation of methylene blue (MB) under UV irradiation. In the case of photo conversion materials, the DSSCs based ZnO nanoplates showed the best performance of photoconversion to electricity at 1.5 AM illumination. Moreover, it also well performed at dye degradation of MB under UV irradiation.

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1. Introduction

Energy shortages and environmental pollution have been investigated in the past two decades. Overcoming shortages of energy and environment problems, there are many works devoted to solve the problems. Since, the solar energy is an alternative energy that can be accessible and easy to utilize. Solar Cell is a general device which can be able to convert the light to the electricity. Nowadays, there are various types of solar cells used in the present day. Dye sensitized solar cells (DSSCs) are promising devices used for photovoltaic conversion due to a low production cost and good conversion efficiency which are maintained under weak indoor light.^{1),2)}

Moreover, due to the growing economy of the world today has caused various environmental pollution problems. For example, the dye business is currently being developed to improve the quality of dye, e.g. to have beautiful colors, and more resistant to various conditions. Therefore, the dye contamination to the water is inevitable.³⁾ There are physical and chemical methods to treat these contaminants.

The use of solar power and semiconductor in the

photocatalytic process, which is widely popular in the removal of organic contaminants.^{3),4)}

Zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor and can be used in many applications, such as photocatalytic, antibacteria, gas sensors, photodetectors and DSSCs.³⁾⁻⁸⁾ A wide varieties of ZnO nanoparticles are depended on the morphological properties and their preparation methods. Various nanostructures of ZnO have been used in fabrication of DSSCs and photocatalysts: nanoparticles, nanospheres, hexagonal disks, hexagonal bilayer disk-like structures, 3D flower-like hierarchitectures, nanowires, nanosheets, tetrapod and nanorods.⁹⁾⁻²¹⁾ However, the effect of NaOH content to the morphology of ZnO to be used as energy harvesting and photocatalytic materials is rarely investigated.

In the present work, ZnO nanoplates and ZnO nanostructure flowers were synthesized in solutions containing different concentrations of NaOH by a cyclic-microwave radiation. Effects of the as-synthesized ZnO with different morphologies with respect to the properties, DSSC and photocatalytic application were discussed in this work.

2. Materials and methods

2.1 Preparation of ZnO samples

Zinc acetate dihydrate (5.0 mmol) and different content of sodium hydroxide (NaOH) were separately dissolved in

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Table 1. ZnO products of the present research

ZnO products	Zn(CH ₃ COO) ₂ ·2H ₂ O (mmol)	NaOH (mmol)
S1	5	none
S2	5	15
S3	5	30
S4	5	45
S5	5	60
S6	5	75

Table 2. Photoanodes of the present research

Photoanodes	ZnO (g)	PEG (g)	Ethanol 95% (ml)	Distilled water (ml)
S2G1	0.35	0.15	0.5	0.5
S3G1	0.35	0.15	0.5	0.5
S4G1	0.35	0.15	0.5	0.5
S5G1	0.35	0.15	0.5	0.5
S6G1	0.35	0.15	0.5	0.5

25 ml of distilled water. They were mixed together and vigorously stirred for 30 min. Details of the products were summarized in **Table 1**. The reaction was cyclically proceeded by 450 W microwave with 5 min on for every 1 min interval for 5 cycles to produce ZnO nanoplates and nanostructure flowers. In the end, the system was left to naturally cool down to room temperature. The products were washed with deionized water and 95% ethanol, and dried at 80°C for 24 h.

2.2 Fabrication of ZnO photoanodes of DSSC

The as-obtained precursor powder was ground in an agate mortar to homogenize ZnO. Sol-gel solutions were prepared by dissolving ZnO and PEG (MW = 20,000 g/mol) in ethanol mixed distilled water and followed by stirring at room temperature for 1.5 h (**Table 2**). To make films, the paste was applied onto a conducting substrate [fluorine-doped tin oxide (FTO)-coated glass, 14 Ω/square, Aldrich] by doctor blading using adhesive scotch tape as a frame (0.5 × 0.5 cm²) and spacer. The tape was pulled out, the films were left to dry at 80°C for 30 min, and as-prepared photoanodes were calcined at 450°C for 1.5 h.

2.3 DSSC fabrication and performance measurement

The ZnO film as a DSSC working electrode was immersed in 0.5 mM solution containing N719 dye (Di-tetrabutylammonium cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II), Sigma-Aldrich) in ethanol for 1 h. To prepare the counter electrode, the platinum (Pt) catalyst (Platisol T, Solarlonix) was coated on a FTO-coated glass by blade coating technique and annealed at 450°C for 30 min. The dye-covered ZnO electrode and Pt-counter electrode were assembled as sandwich type cell and sealed with a suitable ~25 μm thick Surlyn hot-melt gasket. An Iodolyte AN-50 (Solarlonix) electrolyte was injected in between the counter and working electrodes and pinched together for solar cell performance testing.

Photocurrent-voltage characteristics were measured by a computer controlled system under a simulated solar radiation of 100 mW/cm². The performance parameters such as short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and photonic conversion efficiency (η) were determined. Electronic and ionic processes of the DSSCs were tested by an electrochemical impedance spectroscopy (EIS) at a frequency ranging from 1 Hz to 100 kHz.

2.4 Dye-degradation of methylene blue (MB) in ultraviolet (UV) irradiation

The photocatalytic activity of all ZnO were evaluated with a photoreaction system. Typically, the 0.2 g of each ZnO photocatalyst was added to 250 mL of aqueous solution containing MB dye with a concentration of 5 mg/L. Note that the mixed solution was kept in dark for 30 min for the equilibrium of dye adsorption and desorption on the ZnO surface before irradiation. Then, the suspension was exposed to the black light blue (BLB) with wavelength of 375 nm. The reaction solution was stirred. Each sample was taken out at an hour interval.

2.5 Characterization

The products were characterized by an X-ray diffraction (XRD) (Rigaku Miniflex II) equipped with a graphite monochromator of Cu-K α radiation (λ = 0.1542 nm) at a scanning rate of 0.02°/s over the 2 θ range of 10–80°. The presence of ZnO was certified by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F) operating at 15.0 kV beam energy. Spectroscopy absorbance was carried out by a UV-visible spectrometer (SHIMADZU UV 2006).

3. Results and discussion

3.1 Phase and morphology

In this research, no ZnO was synthesized in the NaOH-free solution. In **Fig. 1**, XRD patterns of ZnO synthesized in the solutions containing different contents of NaOH by cyclic-microwave radiation show peaks at 2 θ of 31.683, 34.432, 36.268, 47.533, 56.687, 62.827, 66.344, 67.756 and 69.059° which were respectively indexed to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes of wurtzite ZnO (JCPDS card no.01-080-0075).²² Clearly, the major diffraction peaks of ZnO are at the same position, except for the peak height. The (100) and (200) peaks were almost at the same intensities for the ZnO nanoplates (**Fig. 2**) synthesized in the solutions containing 15 and 30 mmol NaOH. Further increasing the content of NaOH to 45, 60 and 75 mmol, the ZnO nanoplates were transformed into ZnO nanostructure flowers (**Fig. 2**) and the intensity of the (100) peak was strengthened in sequence.

SEM images of ZnO nanoplates and nanostructure flowers are shown in **Fig. 2**. In the solutions containing 15 and 30 mmol NaOH (S2G1 and S3G1), the products were composed of a number of nanoplates orientated in different directions. The plates became larger when more

Fig. 1. XRD patterns of ZnO samples synthesized in the solutions containing different contents of NaOH.

Fig. 2. SEM images of (a, b) ZnO nanoplates of S2G1 and S3G1 and ZnO nanostructure flowers of (c) S4G1, (d–e) S5G1 and (f) S6G1.

NaOH was used, the plates (30 mmol NaOH) > the plates (15 mmol NaOH). When 45, 60 and 75 mmol NaOH were used (S4G1, S5G1 and S6G1), the products were composed of a number of nanorod petals composing the flower-like clusters. The flowers were larger when more NaOH was added.

Top view and side view (cross section) of different ZnO films are shown in Fig. 3. The nanoplates and the nanostructure flowers still retained much of their original

morphologies after coating on FTO by Doctor-blade method. It is to be noted that the film thickness of all the samples (S2G1–S6G1) after calcined at 450°C for 1.5 h are typically of 10.0–15.0 μm height.

3.2 Energy gap

The energy band gap was calculated by assuming that ZnO has a direct type of transition by using the following equation

Fig. 3. SEM images of (a, b) S2G1, (c, d) S3G1, (e) S4G1 and (f) S5G1. (a), (c), and (e) are top view, and (b), (d) and (f) are side view (cross section).

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (1)$$

where α , $h\nu$, A , E_g and n are the absorption coefficient, photonic energy, proportionality constant, energy gap and a constant, respectively. The n pure number decides the type of transition.⁷⁾ The energy band gaps of S2G1, S3G1, S4G1, S5G1 and S6G1 [Fig. 4(a)] were evaluated to be 3.201–3.217 eV.

To estimate the dye-loading capacity, each specimen was immersed separately into a 0.5 M NaOH solution, and afterwards the solution of desorbed dye were evaluated using the UV–visible spectrometer where the absorption spectra of samples were showed in Fig. 4(b). In overall, the adsorption height of dye-desorption were similar which signifies that the occupied dye molecule on the surface are approximately the same in all sample.

3.3 DSSC performance

The effects of different morphologies of ZnO addition to the DSSCs on the electrical properties have been investigated. The DSSCs based on ZnO were fabricated and their electrical properties were compared. Photocurrent-voltage characteristic of the DSSCs were measured, where the DSSC performance was calculated by the following equations

$$\text{Fill Factor : } (FF) = \frac{J_{\max} \cdot V_{\max}}{J_{\text{SC}} \cdot V_{\text{OC}}} \quad (2)$$

$$\text{Efficiency : } \eta(\%) = \frac{J_{\text{SC}} \cdot V_{\text{OC}} \cdot FF}{P_{\text{in}}} \times 100 \quad (3)$$

where $J_{\max}$ and $V_{\max}$ is the current density and voltage at the maximum power (W), J_{SC} is the short-circuit current density, V_{OC} is the open-circuit voltage and P_{in} is the incident power. All measured parameters of the DSSCs are summarized in Table 3.

In Fig. 5(a), the open-circuit photovoltage (V_{OC}) is almost at the same value which are typically 0.52–0.56 V. Results showed noticeable that the current density of each sample are different. The J_{SC} of S2G1 and S3G1 ZnO nanoplates were greater than others. Therefore, it is conceivable that the morphology of ZnO photoanode influenced to the photocurrent. Hence, the greater photocurrent affects to the higher efficiency of DSSCs in this work. The EIS can be further investigated the impedance of DSSCs films.

The analysis of EIS was used to study electron diffusion and the photonic-electric conversion efficiency of DSSCs. The EIS measurement is used to determine the impedance of DSSCs at a frequency range of 0.1 Hz to 100 kHz under one-sun illumination where potential of each measurement was set equal to 10 mV.^{23),24)} The Nyquist plots and the EIS model are represented in Fig. 5(b). The Nyquist plots shows a small semicircle represents the resistance of the redox charge transfer at the counter electrode and the large semicircle refers to the electron transfer resistance at

Fig. 4. (a) The plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for estimation of the direct energy gap of the ZnO films and (b) UV-vis spectra of desorbed dye solution from DSSCs photoanode.

Table 3. Photovoltaic performance of the DSSCs fabricated from ZnO nanoplates and ZnO nanostructure flowers

Samples	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	η (%)
S2G1	9.55	0.52	0.61	3.08
S3G1	9.38	0.56	0.63	3.36
S4G1	3.88	0.56	0.56	1.22
S5G1	6.23	0.56	0.61	2.13
S6G1	5.68	0.54	0.62	1.91

the ZnO/dye/electrolyte interface. The resistance of ZnO/dye/electrolyte interface were fitted as R_{CT} and R_W , whereas R_S represents the sheet resistance of FTO and the contact resistance between FTO and ZnO film.

Figure 5(c) shows the Bode phase plot of EIS spectra display the frequency peaks of the charge transfer at different interface of the DSSCs. The dominant peak frequency at middle frequency (~ 100 Hz) shows the electron transfer process occurred at the ZnO/dye/electrolyte interface. The electron lifetime of the DSSCs is calculated by the following equation.²⁵⁾

$$\tau = \frac{1}{2\pi f_{\max}} \quad (4)$$

where $f_{\max}$ is the peak frequency of a semicircle at the middle frequency region.

Fig. 5. (a) Current density vs. Voltage curves of DSSCs, (b) Nyquist plot and (c) Bode phase plot under one-sun illumination of DSSCs.

In Table 4, all fitted parameters between the experiment data and the EIS model, including calculated electron lifetime are listed in Table 4. The R_S of all components of the fabricated DSSCs were in the range of 17.0–18.8 Ω , while the R_{CT} and R_W of each sample were different. The electron lifetime of all DSSCs based on different ZnO nanostructure were typically 0.77–1.90 s. As a results, the total amount resistance of R_{CT} and R_W are almost a critical role for DSSCs performance. Since, the overall resistance

of DSSCs indicated their performances, the S3G1 sample are the highest performance, following by the S2G1.

In this research, the variation of NaOH used as precursor for ZnO nanostructure synthesis using the microwave method for DSSCs photoanode fabrication yielded two nanostructures, the nanoplate and the nanostructure flowers. The results showed that the DSSCs based on ZnO nanoplate photoanode has better performance than the DSSCs based on ZnO nanostructure flowers.

3.4 Photocatalytic performance

Figure 6 showed the photocatalyst activities under BLB irradiation of the ZnO photocatalysts prepared at different

Table 4. R_s , R_{CT} , R_W and τ of the DSSCs based on ZnO nanoplates and ZnO nanostructure flowers

Samples	R_s (Ω)	R_{CT} (Ω)	R_W (Ω)	τ (ms)
S2G1	17.0	11.8	21.6	1.65
S3G1	17.3	3.84	19.5	1.85
S4G1	18.8	27.3	25.7	0.77
S5G1	18.0	3.52	34.6	1.90
S6G1	18.2	4.60	37.3	1.50

NaOH concentration. The amount of each MB degradation at time interval (C) is to compare with the initial MB concentration (C_0). According to the result, the S2G1 shows the best photocatalytic behavior than others. Within a 5 h, the MB was degraded 90% under UV illumination, approximately. Thus, the different morphologies of ZnO has influenced to the photocatalytic activity.

The effect of NaOH to the synthesis of ZnO was showed in this work. The NaOH concentration determined the surface area of ZnO and morphologies. At the low concentration of NaOH, the ZnO nanoplates was obtained while, the concentration increase, the plates became larger. When the intermediate of NaOH, the ZnO product was composed of a number of nanorod petals composing to the flower-like clusters and the more NaOH added, the size of flower was increased. The morphology of synthesized ZnO influenced on the photoconversion to the electricity of DSSC and also photocatalytic activity.

4. Conclusion

ZnO was successfully synthesized in an alkaline solution under cyclic microwave irradiation. In this work, the

Fig. 6. Degradation curve of MB in the presence of ZnO (a) S2G1, (b) S3G1, (c) S4G1, (e) S5G1, (d) S6G1 and reaction rate ratio (C/C_0) versus irradiation time of UV with different ZnO.

as-obtained ZnO products were hexagonal wurtzite structure of nanoplates and nanostructure flowers. The optimized ZnO nanoplates and ZnO nanostructure flowers were used as photoanodes to fabricate the DSSCs. The EIS results revealed that the DSSC based on ZnO nanostructure flowers and nanoplate had similar electron lifetime. However, the DSSC based on ZnO nanoplate had lower impedance of charge diffusion at ZnO/dye/electrolyte interface than the DSSC based on ZnO nanostructure flower. Among them, the S3G1 ZnO nanoplates based photoanode DSSC exhibited the best photovoltaic conversion efficiency of 3.36%. Moreover, the S3G1 ZnO nanoplates has also a good photocatalytic activity which can be degraded MB by 90%.

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