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4

Zinc Oxide with Visible Light Photocatalytic Activity Originated from Oxygen Vacancy Defects

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Abstract. In this study, ZnO material with oxygen defect was successfully synthesized using a hydrothermal method and interestingly, it was found to possess a remarkable photocatalytic activity under the visible light irradiation. The synthesized ZnO material was then characterized using X-ray diffraction (XRD), diffuse reflectance ultraviolet-visible (DR UV-vis), Fourier transform infrared spectroscopy (FTIR), and spectrofluorometer. Both diffraction pattern and absorption spectrum showed the characteristic of ZnO. However, the maximum emission wavelength of the synthesized ZnO was observed at 558 nm, showing that the ZnO was formed with a high concentration of oxygen vacancy. The excitation spectra also indicated that the prepared ZnO could be excited at the visible light region, which was more than 400 nm. The ZnO was evaluated for photocatalytic phenol degradation under UV and visible light. After 15 hours-reaction, the synthesized ZnO showed the ability to degrade 59.8% phenol under UV light and 39.6% phenol under visible light. This result showed a remarkable performance of ZnO under visible light, which was comparable to that performed under UV light. This study proposed that the existence of oxygen vacancy defects successfully induced the photocatalytic activity of ZnO under visible light irradiation through the electron trapping mechanism in the oxygen vacancy state.

1. Introduction

Organic wastes have caused various types of environmental pollution, including water, soil, and air pollution. The ability of organic compounds to be partially dissolved in water and evaporated into the air makes this waste more difficult to handle [1]. Methods to treat organic wastes include adsorption [2], separation [3], and photomineralization [4]. Photomineralization is a greener approach to handle organic waste as it converts organic wastes into harmless water and carbon dioxide.

Recently, many types of researches are focused on improving the photocatalytic activities of metal oxide photocatalysts. Semiconductors such as titanium dioxide (TiO₂) [5-7] and zinc oxide (ZnO) [8-11] are widely used for this photocatalysis application. Efforts to improve their photocatalytic activities include doping [12,13], dye sensitization [14,15], and the addition of another visible light active semiconductor [16,17]. ZnO is a tremendous potential material with its relatively easy synthesis and ability to harvest UV and visible light if doped or sensitized properly.

Defects in ZnO are usually described as intrinsic and extrinsic defects [18]. Extrinsic defects are introduced through impurities addition, such as nitrogen or metal ion doping [19, 20], while intrinsic defects include interstitial, vacancy, and anti-site defects. The existence of these defects could increase



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photocatalytic activities of ZnO, especially under UV light irradiation [21, 22]. Unfortunately, sunlight consists more of visible light than the UV light. Therefore, in order to utilize the sunlight, improving the activity of ZnO under visible light is very important. In this study, the ZnO was synthesized using a hydrothermal method. The synthesized ZnO was found to possess a remarkable photocatalytic activity under visible light irradiation.

2. Experimental

All chemicals in this research were commercially purchased and used without further treatment.

2.1. ZnO Synthesis

Zinc oxide was synthesized similarly using previously reported method [23]. Zinc acetate dehydrate ($\text{Zn}(\text{CO}_2\text{CH}_3)_2 \cdot 2\text{H}_2\text{O}$, Merck, 99,5–101%) and sodium hydroxide (NaOH, Merck, 99%) were dissolved separately in 75 mL of distilled water at the concentration of 0.1 and 0.2 M, respectively. Zinc acetate solution was then added into the sodium hydroxide solution in a dropwise manner while stirring vigorously. The combined solution was then stirred for an hour to promote zinc hydroxide formation. The resulting solution was moved into a Teflon bottle and was heated using an oven at 150 °C for 6 hours to form ZnO. The ZnO suspension obtained was separated from the byproduct solution through decantation. The ZnO solid was washed with distilled water until the filtrate pH reached neutral. It was then dried to obtain ZnO powder.

2.2. Material Characterization

Synthesized ZnO was characterized using X-ray diffraction (XRD; Rigaku, SmartLab), Fourier-transform infrared spectroscopy (FTIR, JASCO FT/IR-6800), diffuse reflectance ultraviolet-visible (DR UV-vis) spectrophotometer (JASCO V-760), and spectrofluorometer (JASCO F-15500) to study the crystallinity and crystallite size, the functional groups, optical, and fluorescence properties of the prepared samples, respectively. All spectra were recorded at room temperature. As for the FTIR spectra measurement, all the samples were prepared in a pellet form with the addition of potassium bromide (KBr, spectroscopy grade).

2.3. Photocatalytic Test

In the photocatalytic activity test, phenol ($\text{C}_6\text{H}_5\text{OH}$, Merck, 99–100.5%) was used as the organic pollutant model. The light source employed was a halogen lamp (Dolan-Jenner MI-157, 150W). The photocatalyst (50 mg) was suspended into the phenol solution (25 mL, 50 ppm). The mixture was stirred for 2 hours under the dark condition to achieve the adsorption-desorption equilibrium, followed by irradiation using the halogen lamp for 3 hours. The suspension was filtered to remove the solid photocatalyst using a filter membrane prior to the measurement of phenol content using high-performance liquid chromatography (HPLC; Shimadzu, LC-20AT) with C-18 column (YMC-Triart, S-5 μm , 12 nm). The percentage of phenol degradation was calculated from the percentage ratio of degraded phenol concentration to the initial concentration of phenol.

31

3. Result and Discussion

3.1. Structural Analysis

The synthesized ZnO powder was characterized using the XRD. The resulting pattern shows diffraction peaks characteristic to zinc oxide at 2θ of 31.65°, 34.30°, 36.13°, 47.42°, 56.47°, 62.73°, 66.23°, 67.81°, and 68.95° associated with the diffractions of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), and (2 0 1) planes, respectively. Based on the diffraction pattern, ZnO crystalline was successfully synthesized in a wurtzite form with a crystallite size of 32.8 nm.

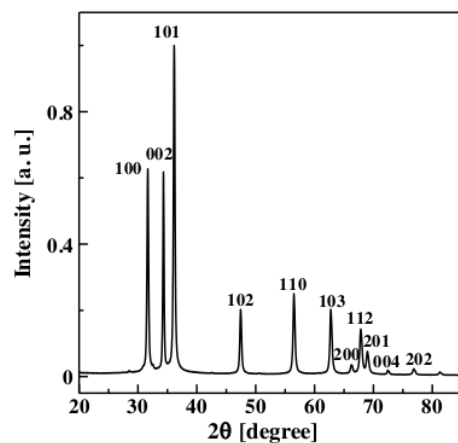


Figure 1. XRD pattern of synthesized ZnO.

3.2. Functional Group Analysis

To clarify further the successful synthesis of ZnO, the changes in functional groups before and after ZnO synthesis were investigated. The spectra of $\text{Zn}(\text{OAc})_2$ as the precursor to synthesize the ZnO and the synthesized ZnO were measured using FTIR spectrophotometer and shown in Figure 2. The $\text{Zn}(\text{OAc})_2$ gave vibrational peaks assigned to the stretching and bending vibrations of O-H of moisture and atmospheric CO_2 , that can be detected at 3106, 2498 and 2348 cm^{-1} . COO^- symmetrical and asymmetric vibrations, C- CH_3 framework, C-C, and acetic ion vibrations can be additionally detected at the wavenumbers of 1563, 1714, 1060, 1018, 846, 690, and 620 cm^{-1} [24]. In contrast, the synthesized ZnO only exhibited peaks at 3400 and 1639 cm^{-1} , corresponding to the stretching and bending vibrations of O-H and H-O-H of water [25], trace leftover of acetic ion at 1639 and 896 cm^{-1} [26], and ZnO vibrational peak at 423 cm^{-1} [27]. The disappearance of acetic ion vibrational peaks indicated the successful ZnO synthesis from the $\text{Zn}(\text{OAc})_2$.

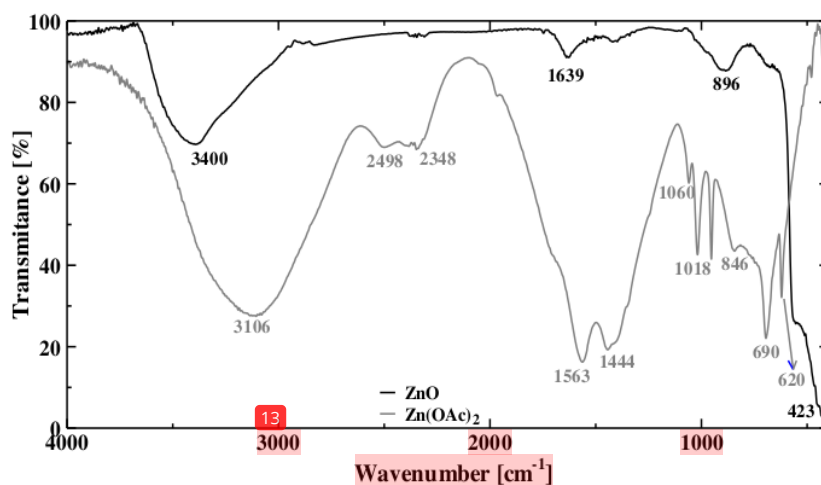


Figure 2. FTIR spectra of $\text{Zn}(\text{OAc})_2$ as the ZnO precursor and synthesized ZnO.

3.3. Optical Properties

The synthesized ZnO was studied for its optical properties by DR UV-vis spectrophotometer. As depicted in Figure 3(a), the ZnO shows an absorption peak at the wavelength of 313 nm, with the absorption edge close to 400 nm. The band gap energy of synthesized ZnO was calculated using the Tauc plot. The obtained determined band gap was 3.22 eV, which was still falling in the UV region (Figure 3(b)).

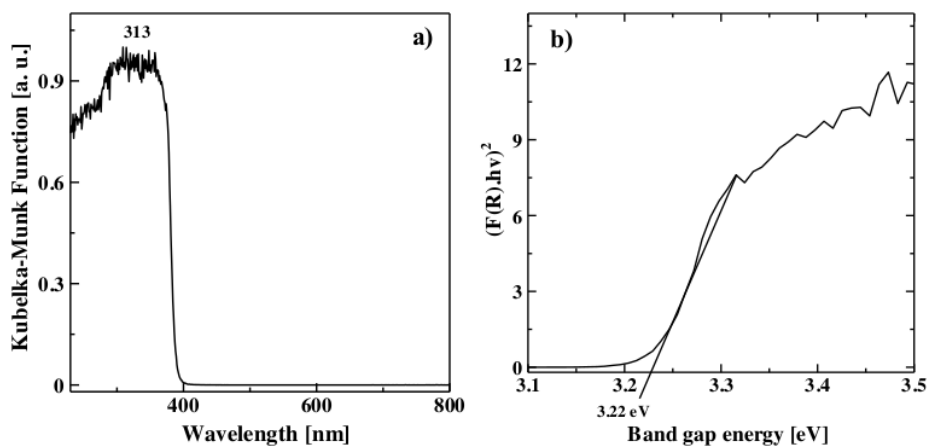


Figure 3. (a) DR UV-vis spectrum and (b) the Tauc plot of synthesized ZnO.

Fig 4 shows the excitation and emission spectra of the synthesized ZnO. The excitation spectrum was measured at the emission wavelength of 558 nm, while emission spectrum was recorded using an excitation wavelength of 372 nm. It has been reported that ZnO prepared by co-precipitation method gave emission peaks at around 420 and 465 nm [28]. Different from this reported sample, the currently synthesized ZnO gave a yellow emission at 558 nm, which was attributed to electron transition from the conduction band (CB) of ZnO to the oxygen vacancy (V_o) [29]. This result indicated the presence of oxygen vacancy defect in the synthesized ZnO.

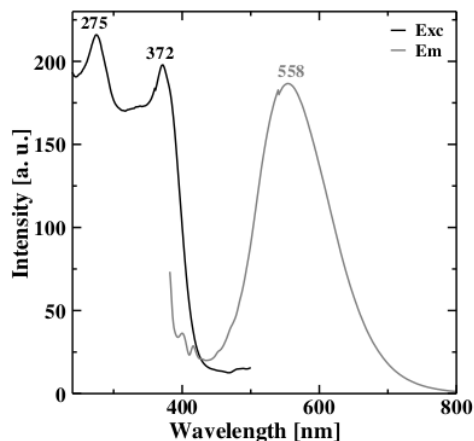


Figure 4. Excitation and emission spectra of synthesized ZnO.

3.4. Photocatalytic Activities

The synthesized ZnO was tested for its photocatalytic activities under UV and visible light irradiation. Figure 5(a) shows the photocatalytic activity of ZnO under UV light irradiation. As shown in Figure 5(a), the amount of left phenol decreased with the increase of the irradiation time. As high as 59.8% of phenol was successfully degraded after 15 hours-reaction. The photocatalytic activity of ZnO under UV light irradiation could be attributed to electron and hole formation, hydroxyl generation, and electron/hole trapping in the oxygen vacancy defect sites [30, 31].

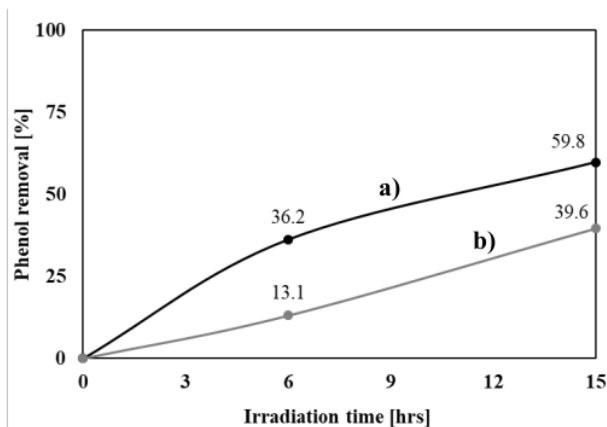


Figure 5. Photocatalytic activity of ZnO under (a) UV and (b) visible light irradiation.

ZnO was also evaluated for its photocatalytic activity under visible light irradiation and the result was shown in Figure 5(b). Contrary to its large band gap of 3.22 eV, the synthesized ZnO showed a remarkable photocatalytic activity under visible light irradiation. After 15 hours-reaction, only falling short of 20% from its photocatalytic activity under UV light irradiation, the ZnO gave 39.6% of phenol degradation. Moreover, comparing the activity of ZnO to other visible-light-active photocatalyst, the currently synthesized ZnO gave a comparable level of photocatalytic activity. For instance, while the ZnO gave 13% phenol degradation after 6-h-reaction, the bulk carbon nitride gave 20% degradation under visible light irradiation [32]. This visible light activity would come from the oxygen vacancy defect as discussed previously. The oxygen vacancy defect would create a new energy level with lower band potential than the conduction band of the ZnO. This lower energy level of the oxygen defects provided the new path for the ZnO to absorb visible light by an electron trapping mechanism in the defect states. The current result was indeed in good agreement with the previous report that the oxygen vacancy led to the enhanced visible light activity of the ZnO [33]. With the presence of the oxygen vacancy defects, the synthesized ZnO was demonstrated to give both UV and visible light activity, which was an important parameter to utilize the whole spectrum of solar light.

4. Conclusion

ZnO was successfully synthesized by the hydrothermal method. XRD patterns showed that ZnO has a crystalline wurtzite structure and a crystallite size of 32.8 nm. FTIR spectra detected the disappearance of acetic acid-related vibration peaks, indicating the formation of ZnO. The fluorescence spectra of the ZnO showed the excitation and emission of oxygen vacancy defect sites in the synthesized ZnO. Photocatalytic tests after 15 hours-reaction showed that the synthesized ZnO has good photocatalytic activity under UV light irradiation (59.8%) and remarkable photocatalytic activity under visible light

irradiation (39.6%). The remarkable photocatalytic activity under visible light irradiation was proposed to be contributed from the oxygen vacancy defect sites.

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