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Synthesis of carbon doped zinc oxide as visible-light driven photocatalyst

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ABSTRACT

Zinc Oxide (ZnO) currently is being used as photocatalyst due to its high photocatalytic activity, low cost and non-toxic. ZnO has great potential to be used as visible light. The band gap of ZnO may be tuned via carbon. In this research, C doped ZnO was synthesized by using microemulsion method. Zinc nitrate, sodium hydroxide, cetyltrimethylammonium bromide (CTAB), cyclohexane, and butanol were used as the precursors for the synthesis of carbon doped ZnO under hydrothermal condition by using an autoclave at 150°C for 1 hour. The solid product was calcined at 300, 400 and 500°C then characterized using UV-vis, FTIR, FESEM and EDX analysis, and XRD. The absorption peaks were obtained to show the present of –OH and –C=O functional groups, respectively. The band gap energy of C doped ZnO was 3.23, 3.22 and 3.21 eV which is correspond to visible light by using diffuse reflectance. In this research, the photocatalysts show hexagonal shape and size of particles about 1.0 to 10µm. The spectrum was confirmed by using EDX analysis. By using XRD pattern, the formation of a single crystal phase Wurtzite structure of ZnO wasdetermined.

Keywords: Zinc Oxide, photocatalystic activity, microemulsion method, hydrothermal condition.

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1. INTRODUCTION

Zinc Oxide (ZnO) generally is being used as photocatalyst due to its high photocatalytic activity, low cost and non- toxic. Furthermore, it is an n-type semiconductor which is possessing wide band gap energy of 3.2 eV. It also easily undergoes an electron-hole pair recombination and photo corrosion in the aqueous environment, which affects the photocatalytic activity of ZnO and it has good activity in photocatalytic degradation of some contaminants than TiO2 due to the band gap value [1,2].

C-doped ZnO is a developing visible-light-responsive photocatalyst with desirable act in cleaning up waste water, water splitting and photoelectrochemical Cells [3,4,5]. Although synthesis of C-doped ZnO has a significant challenge, some methods have been successfully established, including self-doping via thermal decomposition of Zn5(CO3)2(OH)6 as a precursor, pyrolysis of Zn containing inorganic–organic presursors, polymer or carbon templated syntheses, metal organic chemical vapour deposition (MOCVD), and thermal plasma in-flight carbonization methods [6-11].

2. EXPERIMENTAL

In this study the research is intended and directed in three parts. The first part involves the synthesis of zinc oxide and the preparation of carbon-doped zinc oxide. The second part involves the characterization of carbon-doped zinc oxide after calcination at 300, 400 and 500°C. The last part is the photocatalytic activity test of the carbon-doped zinc oxide by the photodegradation of methylene blue in aqueous solution under visible light radiation and photocatalytic activity comparison of carbon-doped zinc oxide at different temperatures of calcination.

For synthesis of carbon-doped ZnO, 1M solution of zinc nitrate was prepared by dissolving 29.74g of Zn(NO3)2·6H2O in 100mL distilled water. 2M sodium hydroxide solution was prepared by dissolving 8g of NaOH in 100mL distilled water. To 28.8mL 1M zinc nitrate, 5.5mL cyclohexane, 8mL butanol, and 5.90g cetyltrimethylammonium bromide (CTAB) were added. In another solution 28.8mL 2M NaOH, 35.5mL cyclohexane, 8mL butanol, and 5.90g CTAB were mixed. Both these solutions were stirred continuously with the help of magnetic stirrer to form clear solutions. These clear solutions were mixed with each other. The mixture was transferred to 250mL Teflon lined autoclave and heated in an oven at 150∘C for 1h. After 1h autoclave was cooled to room temperature. The solid product formed was separated by filtration, washed with distilled water followed by ethanol and finally with acetone, and dried in an oven at 60°C. The hydrothermal product (precursor) thus obtained was characterized using various characterization techniques.

3. RESULTS AND DISCUSSION

3.1 Characterization

The purpose of characterization of the catalyst is to define structural, textural, morphological, and optical and fluorescence properties. In this research, there are four techniques and instruments were used such as Fourier transform infrared spectroscopy (FTIR), Diffuse Reflectance UV-vis (DR-UV), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-Ray Spectroscopy (EDX) and X-Ray Diffraction (XRD). All the techniques are discussed in detail.

3.1.1 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a characterization technique to identify the functional groups present under hydrothermal condition. In this research, carbon doped zinc oxide was studied to determine the functional groups present in the compound under the hydrothermal treatment. FT-IR spectra of the products obtained after calcinations of the precursor at different temperatures for 2 hrs are presented in Figure 1. It shows that the hydrothermal products give the absorption peaks which relates to the O-H stretching and bending vibration of –OH bond. It shows that hydrothermal product is the mixture of Zn(OH)2. In table 1 shows the assignment IR bands for carbon doped ZnO at different temperatures.

Table 1: Assignment of relev ant IR bands of the carbon doped zinc oxide at different temperatures

Assignment	Wavenumber/cm^{-1}		
	C|ZnO (300°C)	C|ZnO (400°C)	C|ZnO (500°C)
OH	3452	3468	3465
OH (bend)	1372	1372	-
C-O (stretching)	1586	1513	-
Zn-O	557	564	553

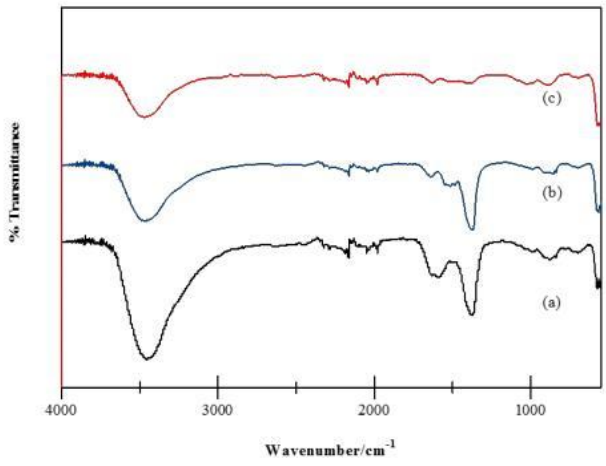


Figure 1: FT-IR of (a) C doped zinc oxide at 300°C, (b) C doped zinc oxide at 400°C, (c) C doped zinc oxide at 400°C

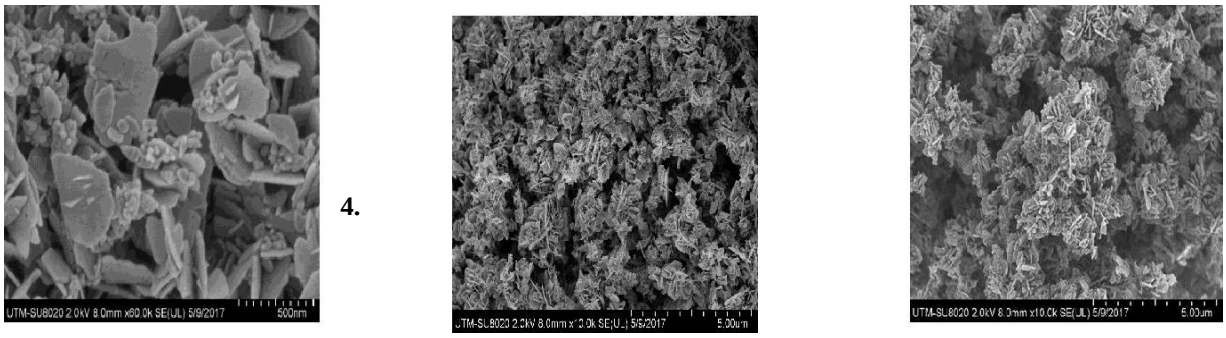
3.1.2 Diffuse Reflectance UV-Vis Spectroscopy (DR-UV)

Figure 2 shows that the DR-UV spectra for photocatalysts at different temperatures. For carbon doped ZnO at temperature 300°C, it gave the absorption peaks at the range 330 and 370 nm. But for carbon doped ZnO at 400°C, gave absorption peaks at 320 and 380 nm, respectively while for carbon doped ZnO at 500°C, the absorption peaks obtained at 330 and 370 nm. This distinct difference in absorption characteristics shows that C is successfully doped on ZnO.

Figure 3 shows that the Tauc plot which was used to estimate the band gap of ZnO obtained at different temperatures. The band gap energy of ZnO obtained at 300, 400 and 500°C was 3.23, 3.22 and 3.21 eV, respectively. Band gap of ZnO obtained at 500°C is less as compared to ZnO obtained at other temperatures because of it absorbs higher wavelength(visible) light. Based on the Figure 4.4, supposing the carbon doped ZnO to be indirect semiconductor, the Tauc plot of (ahv)1/2 versus the energy of absorbed light is obtained.

3.1.3 Field Emission Scanning Electron Microscopy (FESEM) and EDX analysis

Figure 4 represented the FESEM morphology for the carbon doped ZnO calcined at 300,400 and 500°C, respectively. The hydrothermal products obtained from microemulsion method exposed spherical morphology. From the figure, it shows that carbon-doped ZnO obtained are hexagonal in shape and size of particles ranges from 1.0 to 10 µm. The EDX analysis which is used to determine chemical composition of carbon-doped ZnO. Characteristic EDX spectra of C-doped ZnO show the presence of zinc (Zn), carbon (C) and oxygen (O).



4.

(a) C-doped ZnO (300°C) (b) C-doped ZnO (400°C) (c) C-doped ZnO (500°C)

Figure.4: FESEM images for carbon-doped ZnO at different temperatures

3.1.4 X-Ray Diffraction (XRD)

Figure 5 shows a XRD pattern of the C-doped ZnO after calcined at 300,400 and 500°C in 2delta scanning angle in range 20 to 100°. Formation of a single phase Wurtzite crystalline structure of ZnO was obtained (PDF 0 1-0 73 - 876 5). Peaks characterized with Wurtzite crystalline structure of carbon-doped ZnO at 2delta angles of around 29.36, 34.42, 36.22, 56.56 and 62.82° are corresponding to (100), (002), (101), (110) and (103) diffraction planes, separately. XRD pattern of precursor shows that it is the combination of Zn(OH) 2 and as grown ZnO particles

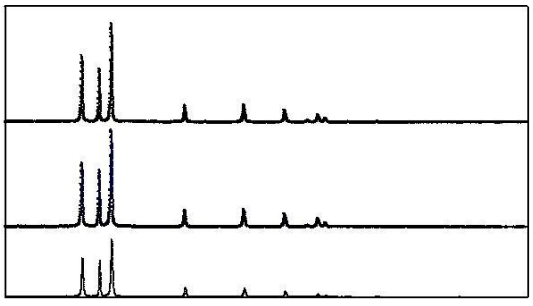


Figure 5: XRD pattern of the (a) C-doped ZnO at 300°C, (b) C-doped ZnO at 400°C and (c) C-doped ZnO at 500°C

4. CONCLUSION

In this research, carbon doped zinc oxide was synthesized by using microemulsion method under hydrothermal condition by using an autoclave at 150°C. Zinc nitrate, sodium hydroxide, cetyltrimethylammonium bromide (CTAB), cyclohexane, and butanol were used as the precursors for the

synthesis of these photocatalysts. The photocatalysts were characterized by using four techniques. In summary, for FT-IR all the carbon doped ZnO which calcined at 300, 400 and 500°C contains hydroxyl groups due to the result of the hydrothermal treatment of water acts as the solvent. Besides that, it found that the photocatalysts recorded the presence of C=O. In DR-UV, the shift of absorption from UV region to the visible region of the carbon-doped ZnO was observed. Tauc plot also shows the narrowing of band gap in carbon-doped ZnO. For FESEM, it shows the shape of photocatalysts were hexagonal and size of particles about 1.0 to 10µm. Thus, the spectrum can be confirmed by using EDX analysis which indicates coexistence of three elements such as Zn, O and C in the photocatalysts.

In conclusion, the spectrum can be observed by using XRD pattern which shows the formation of a single crystal phase Wurtzite crystalline structure of ZnO can be determined.

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