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Effect of drying time on the properties of hydrothermal grown ZnO two-dimensional nanosheets as photocatalysts

Scientific research paper

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ABSTRACT

In this research, a simple and modified hydrothermal method has been used to synthesize two-dimensional zinc oxide nanostructures. Then, the effect of hydrothermal growth time as one of the main post-treatment parameters on the grown structures was investigated. For this purpose, X-ray diffractometry (XRD) and Field emission scanning electron microscopy (FESEM) were utilized to analyze the morphology and crystalline structure of the samples. It was observed that the grown structures have the sheet-like morphology which their thickness decreases with increasing dying time at 80 °C from 9 to 15 h. The XRD results showed that the structures have been crystalized into the hexagonal phase with (101) as the preferred growth orientation. In addition, decrease in the size of the crystallites (calculated from XRD) was concluded with increasing heating time. In the end, the photocatalytic activity of the samples was investigated, and as a result of this investigation, the sample which was heated for 15 h had a better performance in the degradation of methylene blue.

1 Introduction

Zinc oxide (ZnO), which is a direct wide band gap semiconductor, has a hexagonal wurtzite crystal structure at ambient conditions. The tetrahedral coordination of ZnO gives rise to an asymmetric structure that exhibits sp^3 covalent bonding [1]. ZnO has a direct band gap energy of 3.37 eV at room temperature and a large exciton binding energy (60 meV), making it a promising material for several applications such as photo sensors, solar cells, photo catalysis, and so on [2, 3]. Due to surprising properties of nanoscale zinc oxide compared to bulk samples, its applications can be further expanded [4].

Various methods have already been reported on the synthesis of zinc oxide nanosheets with improved chemical and physical properties such as sol-gel method [5], hydrothermal growth method [6], microwave-assisted method [7], anodization method [8], thermal decomposition, and reduction method [9]. Other methods have been reported for the synthesis of zinc oxide nanoparticles, such as micro-emulsion method [10], thermal evaporation [12], chemical mechanical synthesis method [13], spray thermal decomposition [11] and chemical vapor deposition [14]. However, it is difficult to apply most of the mentioned methods in a large-scale production due to complexity, long synthesis process, high reaction temperatures, and involvement of toxic reagents and side products. Compared to these methods, hydrothermal is an attractive candidate for the synthesis of ZnO nanostructures due to its advantages including

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simplicity, easy control and low cost. Nanosheets can be considered as a new class of nanostructured materials which provide an anisotropic structure with a nanometer-scale thickness [15].

About half of the dyes which are used in industries like food and textile are azo compounds. Effluents from these industries enter a considerable amount of the azo dyes into the environment which may cause mutagenic and carcinogenic hazards [16]. MB is a toxic, carcinogenic, and non-biodegradable dye which is harmful to the human health and environment. Thus, its removal through cost-effective and environment-friendly methods should be developed. Photocatalysis has been well known for dye degradation. Photocatalyst is composed of two words, photon and catalyst, which is a substance that changes the speed of the reaction. As a result, a photocatalyst is a substance that changes the reaction rate in the presence of light. Most of photocatalysts are basically semiconductors. During photocatalytic process, an electron-hole pair is created by exposing a semiconductor material to light which participate in the degradation reactions.

The discovery of two-dimensional (2D) materials has shown great promise in the field of photocatalysis so that the use of two-dimensional materials as photocatalyst increases photocatalytic activity [17]. In two-dimensional materials, the electrons in the compound or alloys are confined in a plane. A wide range of 2D materials including phosphorene, MXenes, transition metal dichalcogenides (TMDs) and many other monolayer materials have been exfoliated from their bulk [18]. ZnO nanosheets possess high mechanical stability, large effective surface area, and ability to be produced at temperatures lower than the boiling point of water which make them interesting [19].

Herein, we synthesize a two-dimensional structure of zinc oxide nanosheets using a simple hydrothermal method, and investigate the effect of the annealing duration time as a main parameter on the prepared structures. Then, photocatalytic performance of the grown structures for degradation of Methylene blue (MB) upon UV irradiation will be measured.

2 Materials and methods

Urea, deionized water, zinc chloride, and ethanol with analytical reagent grade were used as the precursor materials. Hydrothermal method was used for the synthesis of ZnO nanosheets. For this purpose, 0.960 g of urea and 0.109 g of zinc chloride with addition of deionized water were mixed on a magnetic stirrer for 10 min. Then, glass substrates (1×1 cm^2) were put in an autoclave containing 20 ml of the prepared solution. The autoclave was heated at 80 ℃ in an oven for 24 h. After hydrothermal process, the formed layers on the glass substrates were scratched and washed with DI water and dried for 9, 12, 15 h at 80 ℃ in the oven. At the end, an annealing at 300 ℃ for 30 min in a furnace was performed for all samples.

The structure and morphology of the grown structures were characterized through a scanning electron microscopy (SEM; VEGA3 model, TESCAN company) and an X-ray diffractometer (XRD; Ultimo IV, Rigaku company). To evaluate photocatalytic activity, 10 mg/L aqueous solution of methylene blue was used for degradation. At first, the sample absorption process was carried out in the dark for 1 h. Then, the photo degradation test was performed for 150 min with sampling every 30 min under UV illumination. A UV-Vis spectrophotometer (Ocean Optics, HR4000) was used to measure the absorption of the dye-polluted water solution during photocatalytic process.

3 Results and discussion

3.1 Morphology and structure

The morphology of the synthesized samples was characterized using SEM. As shown in Figs. 1-3, formation of sheet-like nanostructures is observed in all samples. The enlarged images show that ZnO nanosheets with rough surfaces are assembled into 3D configuration which form a porous structure. The average thickness of the nanosheets is different which is 49, 47, and 35 nm for the samples dried for 9, 12, and 15 h, respectively. Therefore, with increasing drying duration from 9 to 15 h, average thickness of the nanosheets decreases. Formation of flower-like structures from the nanosheets provide a 3D configuration with a high effective surface area which is beneficial for the photocatalytic activity.

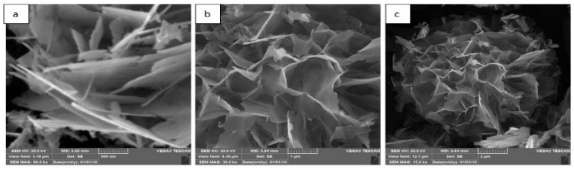

Figure 1. (a-c) SEM images of the sample with the annealing duration of 9 h.

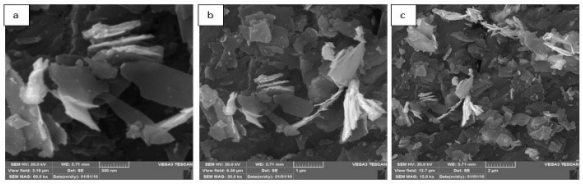

Figure 2. (a-c) SEM images of the sample with the annealing duration of 12 h.

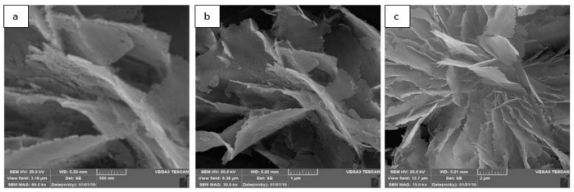

Figure 3. (a-c) SEM images of the sample with annealing duration of 15 h.

Figure 4 shows XRD patterns of the samples. The existence of the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) crystalline planes show that the dominant crystalline phase is wurtzite (card No. 01-079-0208). No characteristic peaks were observed for any other impurities, indicating that all precursors were converted to ZnO completely. The crystallite size was calculated from Scherer's equation [20]:

$$D = 0.89\lambda/\beta\cos\theta, \quad (1)$$

where D is the average crystallite size in nanometers, λ is the X-ray wavelength (1.5406 Å), β is full width at half maximum (FWHM) of the peak and θ is the corresponding Bragg diffraction angle. The crystallite size for the 9, 12, and 15 h samples were obtained 141, 70, and 21 nm, respectively considering the (101) peak being the preferred orientation for all the samples. Zhou et al. used density of states calculations to determine the electron energy of the ZnO crystalline planes. The results indicated that the electron energy of the (101) plane is lower than that of the (002) plane. This shows that (101) plane possess better catalytic properties [21]. Herein, dominancy of the (101) planes confirms suitability of the synthesized structures for catalytic applications.

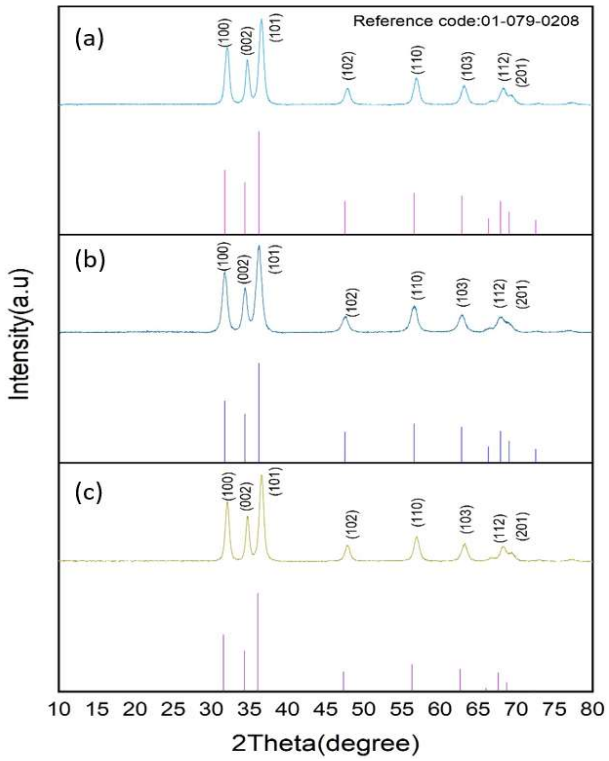

Figure 4: Comparison of XRD spectra of three samples annealed for: a) 9 h, b) 12 h, and c) 15 h.

During hydrothermal process, crystal nucleation followed by nucleation growth occurs. drying step can play an important role in the formation of nanosheets. In the synthesis process, a solution containing mineral precursors is usually used, which turns into nanosheets composed of necessary precursors for formation of ZnO. Then, duration of drying process affects the properties and characteristics of zinc oxide nanosheets including size and shape of the nanosheets. After annealing at furnace, theses precursors convert to ZnO.

3.2 Photocatalytic activity

Here, regarding the phase of ZnO and pollutant, photocatalytic reactions are considered heterogeneous. Figure 5 shows absorbance spectra of MB solution exposed to the synthesized ZnO nanosheet structures which have been annealed for different duration of time

upon exposure to UV. There are four steps in the photocatalysis mechanism on the zinc oxide surface as follows [22]:

(1) charge carrier production, (2) charge carrier trapping, (3) charge carrier recombination, and (4) photocatalytic degradation of organic pollutants.

(1) charge carrier production:

By irradiating ZnO with UV, the electrons are excited from the valence band to the conduction band. The excitation of the electrons creates a positive hole in the valence band and thus, generally an electron-hole pair (e^--h^+) is created;

$$ZnO + h\nu(UV) \rightarrow ZnO(h^+ + e^-)$$

(2) charge carrier trapping:

The e^-- h^+ pairs are trapped by the electron and hole traps and recombination is prevented. Positive holes are a strong oxidizing agent that can directly oxidize adsorbed pollutants or react with electron donors such as water (H_2O) or hydroxyl ion (OH^-) to form the hydroxyl radical ($\dot{O}H$), which is a strong oxidizing agent.

$$h^+ + H_2O \rightarrow \dot{O}H + H^+$$

$$h^+ + OH^- \rightarrow \dot{O}H$$

On the other hand, the electron trapped in the conduction band must be inhibited by an electron acceptor to suppress its recombination with the trapped hole. One of the electron acceptors is oxygen (O_2). By reducing O_2 with electrons, active superoxide radical anions ($O_2^{\cdot-}$) are produced, as well as other oxidizing species such as hydroperoxyl radicals ($HO_2^{\cdot}$) and hydrogen peroxide (H_2O_2). Excess OH radicals are produced through the following reactions [16, 23]:

$$O_2 + e^- \rightarrow \dot{O_2^-}$$

$$\dot{O_2^-} + H^+ \rightarrow \dot{HO_2}$$

$$\dot{O_2^-} + \dot{HO_2} \rightarrow HO_2^- + O^-$$

$$2\dot{HO_2} \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + \dot{O_2^-} \rightarrow OH^- + \dot{O}H + O_2$$

$$H_2O_2 + e^- \rightarrow OH^- + \dot{O}H$$

$$H_2O_2 + h\nu \rightarrow 2\dot{O}H$$

(3) charge carrier recombination:

In competition with charge transfer to adsorbed contaminants, there is an opportunity for recombination of both e^--h^+ pairs and trapped carriers. The recombination can occur in the bulk or on the surface of the photocatalyst with releasing heat.

$$e^- + h^+ \rightarrow ZnO + heat$$

(4) photocatalytic degradation of organic pollutants.

Essentially, $\dot{O}H$, $HO_2^{\cdot}$ and $O_2^{\cdot-}$ radicals as well as photogenerated holes (h^+) are highly reactive intermediates that will attack repeatedly in the reacting system and ultimately lead to complete mineralization of the organic pollutants.

The reason for the different performance of photocatalytic degradation can depend on the factors such as the thickness of nanosheets, the effective specific surface area, the size of nanoparticles, and higher density of defects as electron trapping centers**.** One of the important factors to determine which of the samples had a better photocatalytic performance is the effective surface area. The SEM images with the same scale (2 μm scale bar) in Figs. 1-3 show that the sample dried for 15 h composed of nanosheets with higher exposed surface. The sheets in 15 h dried sample are thinner than those of other samples. In addition, they have been arranged in the form of flowerlike structures. This prevents overlapping of the sheets for effective exposure to the dye pollutant solution.

The ratio of final concentration (C) to initial concentration (C_0) which were obtained from the absorption spectra was calculated as presented in Fig. 6. It is seen that the 12 h and 15 h dried samples possess the highest and lowest photocatalytic activity, respectively.

Comparing the photocatalytic efficiency through this relationship, $[(C_0\text{-}C)/C_0]\times100$ (where C_0 and C are the initial and final concentrations) as shown in Fig. 6, values of 75, 57.9, and 83.2 were achieved for 9, 12, and 15 h dried samples, respectively. Conclusively, among three samples, the sample dried for 15 h showed better performance for degradation of MB. In addition, the lowest efficiency of 12 h dried sample could confirm the effectiveness of flowerlike structures in photocatalytic performance.

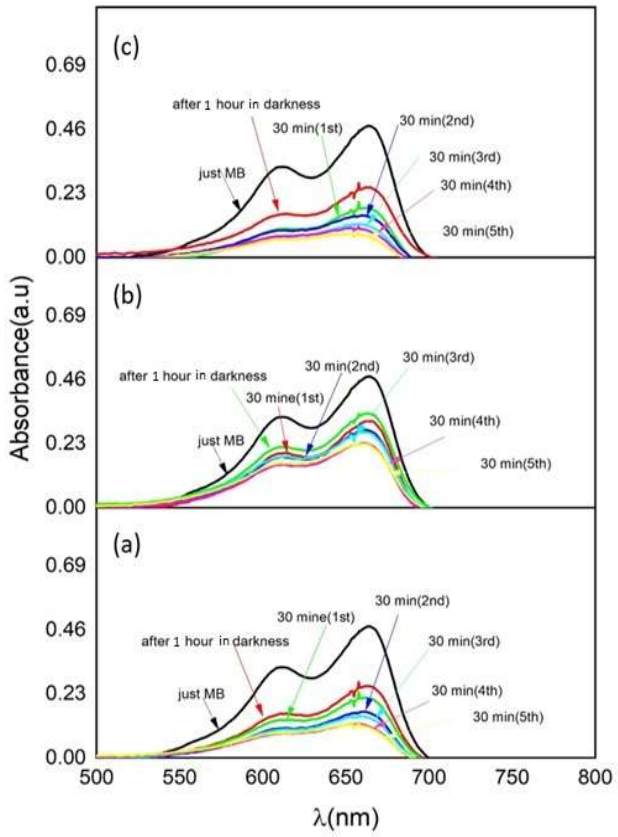

Figure 5. Photocatalytic absorption spectra for samples dried for a) 9, b)12 and c)15 h.

F. Al-Hazmi et al. [23] reported degradation of MB with two dimensional nanosheets synthesized by a microwave hydrothermal method. The samples showed an almost complete degradation of MB within 50 min. They used ZnO nanosheets in the form of powder. They used MB solution with lower concertation compared to this research. Rafaie et al. investigated the effect of different amounts of ZnO powder as a photocatalyst for photo degradation of MB solution. A 96.2% percent degradation of MB was achieved after 60 min for 10 mg of ZnO powder [24]. In both of the mentioned papers, MB solution with lower concertation compared to this research was used.

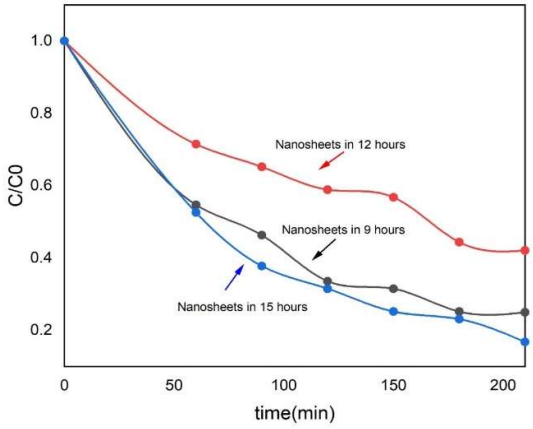

Figure 6. Comparison of photocatalytic degradation concentration of the samples.

Conclusions

In summary, based on a hydrothermal, low-temperature (80 °C), environmentally friendly (without any surfactant or organic solvent) method, two-dimensional ZnO nanosheets were successfully synthesized. The synthesized structures were examined by various techniques. According to the SEM images, all three samples consist of 2D nanosheets which have been arranged in a three-dimensional network architecture. It resembles to flower-like structures in 9 and 15 h dried samples. Furthermore, XRD results showed that increasing the drying time decreases the crystallite size of the prepared ZnO nanosheets. The samples were used as a photocatalyst for degradation of MB solution. The obtained results showed that the sample dried for 15 h possesses highest performance compared to the other samples.

Acknowledgements

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