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The photocatalytic activity of ZnO prepared by simple thermal decomposition method at various temperatures

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ABSTRACT

Nanorods of pure ZnO were synthesized by simple thermal decomposition method. The ZnO is prepared by direct calcination of zinc acetate dihydrate. The hexagonal structure of ZnO is confirmed by X-ray diffraction. The nanorods shape and size have been identified through SEM and TEM analyses. The surface component and the oxidation states of ZnO sample were investigated using XPS. The calculated bandgap values of ZnO suggest that the photocatalytic activity may be good under UV light irradiation.

1. Introduction

The broad range of chemical contaminants produced by industry and agricultural activities has become an important issue that affects the ecological safety. People are exposed to a spectrum of pollutants present within the environment. The major pollution which affects the environment is water pollution. The harmful effluents from textile and other industries are released directly or indirectly into water sources [1–22]. One of the best ways to reduce contamination of water is by photocatalytic treatment. Photocatalysis is a unique process for rectifying energy and environmental issues. During the last two decades, semiconductor metal oxides and sulphides were mostly used in photocatalytic activity.

Zinc oxide (ZnO) is a functional semiconducting material that has interesting properties such as non-hazardous, good chemical and thermal stability. In addition, ZnO has shown a great deal of research interest in the field of catalysts, sensors, DSSCs and antibacterial due to some of its fascinating properties. ZnO has received a considerable attention as a cost effective alternative to other oxides [23–26]. Number of methods has been used to synthesize various nanostructures of ZnO including the hydrothermal process, vapour phase growth, chemical solution route, thermal evaporation, sol–gel process, etc. ZnO has been synthesized with a variety of well defined nanostructures with various morphologies such as nanospheres [27], nanowires [28], nanorods [29], nanonails [30] and nanobridges [30].

In this paper, ZnO is prepared by simple thermal decomposition method at different temperatures. The prepared samples were characterized by various physical and chemical techniques. Finally ZnO samples were used as a catalyst to degrade the organic pollutants. The degradation efficiency of the ZnO samples prepared at three different temperatures was compared and the results are discussed in detail.

2. Materials and methods

Zinc acetate dihydrate (Rankem) used in the present study was of analytical reagent grade without further purification. Methylene blue (MB) and methyl orange (MO) were purchased from Aldrich chemicals. All aqueous solutions were prepared by using double distilled water.

2.1. Thermal decomposition method

Thermogravimetric analysis (TGA) was first performed using zinc acetate dihydrate for a better understanding of its thermal stability and decomposition temperature. The samples were analysed with a heating rate of 10 °C per minute. The TGA thermogram of zinc acetate dihydrate at the temperature range of 50–700 °C is shown in Fig. 1.

Initial weight loss of 16% at 170 °C is due to dehydration, yielding anhydrous zinc acetate. A weight loss of 52%, in the range of 171–312 °C indicated the decomposition of acetate and the formation of zinc oxide. This helped to determine the residual zinc oxide value

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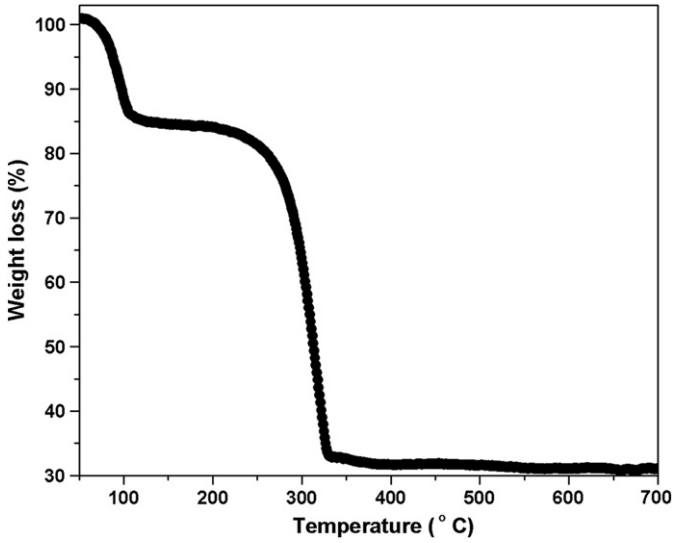

Fig. 1. Thermogravimetric analyses for zinc acetate dehydrate.

of 32% which coincided with the calculated theoretical residual value of 37.5% when ZnO was the only residue. The 5.5% weight difference is due to the sublimation of zinc acetate species or zinc organic composition such as $Zn_4O(CH_3CO_2)_6$ [31–33]. There was no further decomposition beyond 312 °C. The process resulted in the synthesis of ZnO with the total weight loss being 68%. The decomposition temperature determined in this analysis was used for fixing the temperature for the synthesis of ZnO.

5.0 g of zinc acetate dihydrate was taken in the mortar and ground well for 1 h then the powder was calcined in an alumina crucible at different temperatures 350 °C, 650 °C and 950 °C for 3 h. The ZnO were formed by the following chemical reaction.

$$Zn(CH_3COO)_2 \cdot 2H_2O \xrightarrow{\Delta} Zn(CH_3COO)_2 + 2H_2O\uparrow \quad (1)$$

$$4Zn(CH_3COO)_2 + 2H_2O \xrightarrow{\Delta} Zn_4O(CH_3COO)_6 + 2CH_3COOH\uparrow \quad (2)$$

$$Zn_4O(CH_3COO)_6 + 3H_2O \xrightarrow{\Delta} 4ZnO + 2CH_3COOH\uparrow \quad (3)$$

$$Zn_4O(CH_3COO)_6 \xrightarrow{\Delta} 4ZnO + 2CH_3COOH\uparrow + 3CO_2\uparrow \quad (4)$$

2.2. Self designed UV light photocatalytic reactor

The experiment was carried out in a 600 mL capacity borosilicate cylindrical beaker surrounded by water jacket. The beaker placed on a magnetic stirrer. There was an additional opening in the cylindrical beaker for collection of solution from the reactor from time to time. During the irradiation time, the reaction was maintained at 30 °C to 33 °C temperature with the help of water circulation continuously through the double-walled water jocket (preventing from thermal catalytic effect). The cylindrical beaker completely wrapped by an aluminium foil for reflect UV light irradiation of back into the solution and exerting the outer wall of the reaction. The radiation source was a low-pressure 8 W mercury vapour lamp emitting ultraviolet (UV) radiation with a wave length of 365 nm. The lamp was installed into a quartz glass tube and fitted the inner cylindrical beaker with use of lid. The quartz glass tube acted as sheathes of the lamp and to protect it from direct contact with the aqueous solution. The detailed schematic view of the experimental set-up is illustrated in Fig. 2.

The complete reactor setup is maintained in dark box. Power supply to the UV lamp is controlled by a timer circuit so that the lamp will get on and off automatically after every irradiation time intervals.

2.3. Photocatalytic testing

In order to show their potential environmental application for the degradation of two water soluble dyes such as methylene blue (MB) and methyl orange (MO) using ZnO catalyst under UV light irradiation. Reaction suspensions were prepared by adding 500 mg catalyst into 500 mL of MB/MO solution with an initial concentration of 3×10^{-5} mol/l. Before photocatalytic run was started, the aqueous suspension containing MB/MO and the catalyst were stirred under dark conditions without light illumination and found that the aqueous suspension did not change the colour. When the UV light was irradiated in the absence of ZnO, still there was no change in the colour of dye. Therefore, the presence of both irradiation and ZnO was essential for the efficient degradation. During the photocatalytic experiments, the reaction mixtures were stirred for 30 min under dark condition to establish adsorption–desorption equilibrium condition. The samples from the suspension were collected at regular intervals of time, centrifuged and filtered. The concentration of MB and MO in each sample was analysed using UV–visible spectrophotometer at a wavelength of 664 and 464 nm respectively. All UV–visible

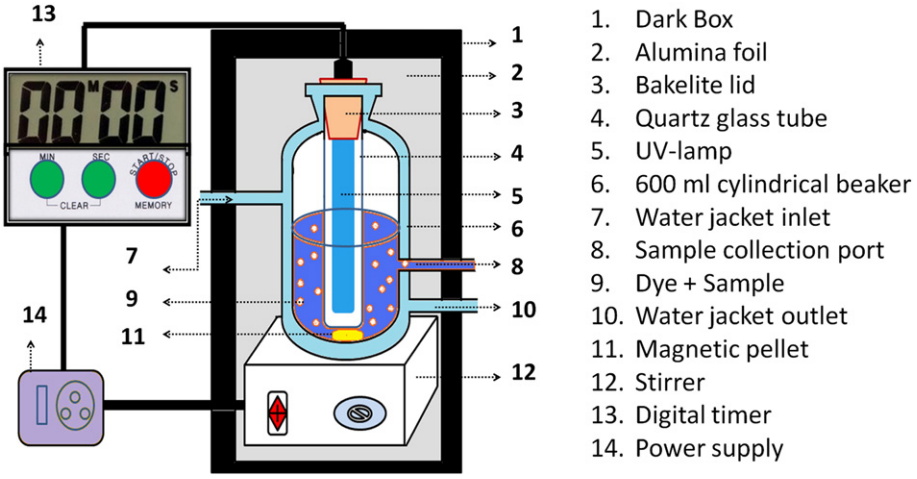

Fig. 2. Schematic diagram of the UV-light photocatalytic experimental set-up.