Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Solution combustion synthesis of ZnO powders using CTAB as fuel

H. Vahdat Vasei, S.M. Masoudpanah*, M. Adeli, M.R. Aboutalebi

School of Metallurgy & Materials Engineering, Iran University of Science and Technology (IUST), Tehran, Iran

ARTICLE INFO

Keywords:
ZnO
Solution combustion synthesis
CTAB
Specific surface area
Photocatalytic activity

ABSTRACT

Zinc oxide (ZnO) powders have been prepared by solution combustion synthesis method using cetyltrimethylammonium bromide (CTAB) as fuel. The effects of fuel to oxidant ratios ($\phi = 0.5, 0.75, 1$ and 1.5) on the combustion behavior, phase evolution, microstructure, optical properties and photocatalytic performance were investigated by thermal analysis, X-ray diffractometry, electron microscopy, and diffuse reflectance spectrometry techniques. The slow decomposition rate of CTAB guaranteed the direct formation of single phase and well-crystalline ZnO powders regardless of fuel content. The specific surface area of the as-combusted ZnO powders with platelet particles increased from 21 ± 1 to 35 ± 2 m^2/g with fuel content. The band gap energy also increased from 2.99 to 3.13 eV due to the decrease of particle size. The as-combusted ZnO powders at $\phi = 1.5$ exhibited the highest photodegradation (~69%) of methylene blue under ultraviolet light irradiation, due to their good crystallinity and smaller particle size.

1. Introduction

Zinc oxide (ZnO) is an interesting material for many applications such as electro-optics, spintronics and gas sensors, due to its wide band gap (3.27 eV), large exciton binding energy (60 meV), cost effectiveness, nontoxicity, and structural stability [1–3]. The physical and chemical properties of ZnO strongly depend on structure, particle size and shape and composition which are tunable via synthesis method [4]. Zinc oxide powders have been prepared by various routes such as solid state, hydrothermal, precipitation, solvothermal, solution combustion synthesis, etc. [5–9]. Among the methods, solution combustion synthesis (SCS) as a simple, versatile, time- and energy-efficient and environmentally friendly route has received a great attention for rapid and mass production of nanomaterials [10]. SCS involves a self-sustained exothermic reaction between oxidizers (e. g. metal nitrates) and organic fuels (e. g. urea, glycine, citric acid) [11]. The molecular mixing of cations together with released heat by combustion reaction guarantee the formation of complicated structures at low temperatures [12]. Furthermore, the combustion of organic fuels generates a large amount of gaseous products such as CO_2, H_2O, H_2, N_2, CO, etc., leading to porous structures. The outgoing gases rapidly cool the as-combusted products, preventing particle growth and sintering [13–15].

Powder characteristics of the as-combusted ZnO powders such as structure, particle size and shape, specific surface area and optical properties can be mainly tuned by fuel nature and fuel content, metal precursor, pH, gel rheology, etc. [16,17]. Urea and glycine are popular fuels in SCS for their low decomposition temperature, high solubility, readily available and low cost [18,19]. However, other organic fuels such as oxalic acid, dextrose, oxalyl dihydrazide, L-Glutamine, Leucine, L-Valine, etc. were also employed for solution combustion synthesis to improve the specific surface area and crystallinity of the as-combusted ZnO powders [20,21]. Cetyltrimethylammonium bromide (CTAB) as a cationic surfactant has been widely employed in material synthesis to reduce particle size by capping or protecting [22]. CTAB has been used in solution combustion synthesis of oxide nanoparticles such as CuO [23], Co_3O_4 [24], $SrFe_{12}O_{19}$ [25], $BiVO_4$ [22]. Bedi and Singh compared the effects of CTAB on the morphology and particle size of the as-combusted CuO powders [26]. The surfactant molecules separate the sol particle due to the electrostatic stabilization, leading to spherical CuO nanoparticles (~20 nm) with a minimum degree of agglomeration.

In the present work, the effects of fuel to oxidant ratio on the combustion behavior, phase, microstructure, optical properties and photocatalytic activity of the solution combusted ZnO powders using CTAB as fuel were reported. The slow combustion reaction rate of CTAB fuel led to the formation of small platelet ZnO particles at high fuel content.

2. Experimental procedures

The required amounts of zinc nitrate ($Zn(NO_3)_2$) and cetyltrimethylammonium bromide ($[(C_{16}H_{33})N(CH_3)_3]Br$) as fuel were dissolved in distilled water in which the different fuel to oxidant ratios ($\phi = 0.5, 0.75, 1$ and 1.5) were used. After homogenization, the precursor

---

* Corresponding author.
E-mail address: masoodpanah@iust.ac.ir (S.M. Masoudpanah).

https://doi.org/10.1016/j.ceramint.2018.01.202
Received 25 December 2017; Received in revised form 24 January 2018; Accepted 24 January 2018

Please cite this article as: Vahdat Vasei, H., Ceramics International (2018), https://doi.org/10.1016/j.ceramint.2018.01.202

solution was poured into a dish and heated till to transform into a gel while by further heating up to 250 °C on a hot plate, ignition reaction started from a point and propagated spontaneously. The resulted powders were hand-crushed with a pestle.

IR spectra in the range of 400–4000 cm^{-1} were measured by Fourier transform infrared (FTIR) spectrometer (8500 SHIMADZU). Thermal decomposition of the dried gels at 80 °C was examined by simultaneous differential thermal and thermogravity analysis (DTA/TGA) in air with the heating rate of 5 °C/min in a STA BäHR 503 instrument.

Phase evolution was analyzed by PANalytical X-ray diffractometer (XRD) using monochromatic CuKα radiation. The XRD patterns were also submitted to a crystal structure analysis by the Rietveld method using High score plus software. The morphology and microstructure of the powders were observed by TESCAN Vega II field emission scanning electron microscopy.

The Brunauer–Emmett–Teller (BET) specific surface area of the powders was measured by the nitrogen gas adsorption technique using a PHS-1020 instrument at 77 K, once the samples were degassed at 250 °C for 5 h. BJH (Barrett–Joyner–Halenda) cumulative volume of pores was calculated from the adsorption branch of the isotherms.

The UV–Vis diffuse reflectance spectra were recorded on a Shimadzu UV–Vis-52550 spectrophotometer in the wavelength range of 200–700 nm.

Photocatalytic activity of the as-combusted ZnO powders was evaluated by degradation of methylene blue (MB) in aqueous solution under ultraviolet (UV) light radiation. Two UV lamps (8 W) were employed as light source. In each experiment, 0.1 g of catalyst was added into 100 mL of methylene blue solution with a concentration of 15 mg/l. Furthermore, the pH of solution was adjusted to 2 by adding HCl. The suspension was stirred in dark for 60 min to establish the adsorption/desorption equilibrium, then the solution was illuminated under UV light irradiation. At appropriate time intervals, about 5 mL of suspension was sampled and the solid phase was separated from the solution by centrifugation at 4000 rpm for 20 min. The concentration of each degraded solution was monitored on PG Instruments Ltd T80-UV/Vis spectrophotometer.

3. Results and discussion

On the base of propellant chemistry, the redox reaction during combustion process by considering CO_2, N_2, Br_2 and H_2O as byproducts can be written as follows [27]:

$$Zn(NO_3)_2 + \frac{10\varphi}{118}C_{19}H_{42}BrN + \frac{5}{2}(\varphi-1)O_2 \rightarrow ZnO + \frac{190\varphi}{118}CO_2 + \frac{210\varphi}{118}H_2O + \frac{5\varphi}{118}N_2 + \frac{5\varphi}{118}Br_2 \quad (1)$$

Here, the stoichiometric mixture ($\phi = 1$) means no need to atmospheric oxygen for completing fuel oxidation, while the $\phi > 1$ (or $\phi < 1$) corresponds to the fuel-rich (fuel-lean) condition.

FTIR spectra of the dried gels at 80 °C and the as-combusted ZnO powders prepared at $\phi = 1$ are shown in Fig. 1. For the dried gel, the broad band at 3200 − 3800 cm^{-1} is due to the hydroxyl groups originating from organic phases and residual water [28]. The bands at 2920 and 2852 cm^{-1} are related to the stretching vibration of C-H bonds [29]. The CO_2 group on the metallic cations leads to the absorption band at 2360 cm^{-1} [29]. The absorption bands at 1388, 1355, 827 and 665 cm^{-1} can be assigned to the NO_3^- groups which demonstrate that the NO_3^- exists as a group in the structure of gel during the gelation of solution formed from nitrates and CTAB fuel [30]. The direct formation of ZnO following combustion reaction can be confirmed by the absorption bands in the range of 400–600 cm^{-1} for stretching vibration of Zn-O bonds [31]. The absorption bands at 3200 − 3800 cm^{-1} and 1641, 1550 and 908 cm^{-1} are related to the physisorbed hydroxyl groups and residual organics on the surface of the ZnO powders, respectively [32].

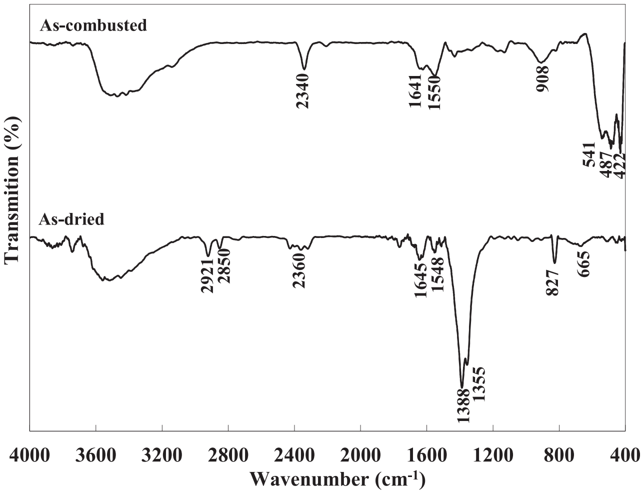

Fig. 1. FTIR spectra of the dried gel and the as-combusted ZnO powders prepared at $\phi = 1$.

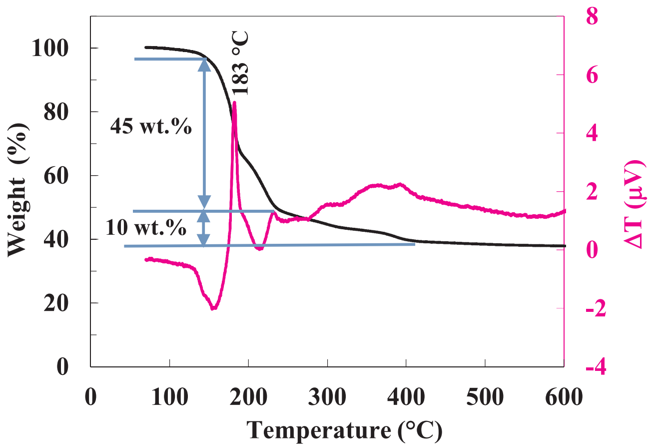

Fig. 2. TGA/DTA curves of the dried gel prepared by CTAB fuel at fuel to oxidant ratio of 1.

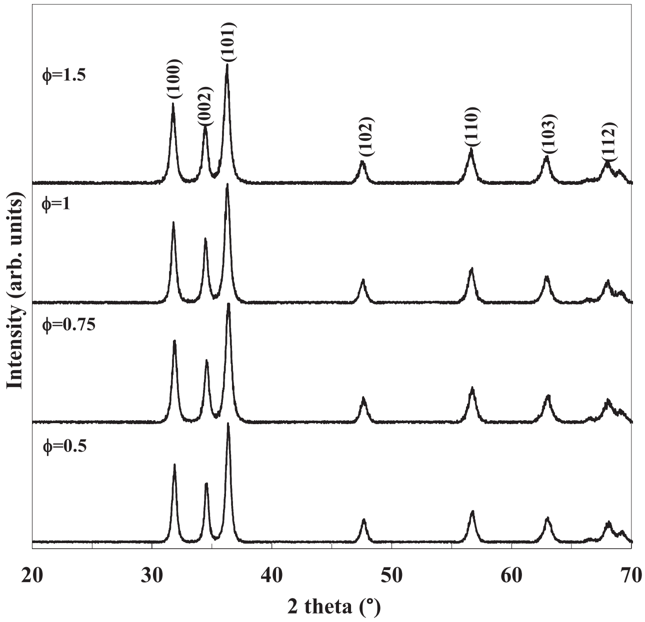

Fig. 3. XRD patterns of the as-combusted ZnO powders at various ϕ values.