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Original Research Paper

The effect of fuel and fuel-oxidizer combinations on ZnO nanoparticles synthesized by solution combustion technique

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ABSTRACT

We report on the synthesis of nanocrystalline ZnO particles by solution combustion technique using new organic fuels such as L-Glutamine, Leucine and L-Valine. The thermal decomposition and combustion of nitrate-organic fuels (precursors) were investigated through TG-DTA and XRD techniques. The results show that, the nitrate-organic fuel (precursor) gels exhibit self-propagating behavior at 400 °C after ignition in air. The effect of fuel and fuel to oxidizer ratio on structural properties of as-synthesized ZnO powder was investigated. It was observed that, the particle size of as-synthesized ZnO powder depends on F/O ratio, which influences the combustion process. The detailed analysis on the structure of as-synthesized ZnO powder was carried out by Rietveld refinement on XRD data and through TEM studies. Further, adiabatic temperature (T_{ad}) was calculated through thermodynamic theoretical calculations for different fuel to oxidizer ratios. The results were discussed on the basis of the correlations established between the T_{ad}, nature of the combustion and structural properties of the resulting powders.

1. Introduction

Zinc Oxide, ZnO, is one of the wide band gap inorganic semiconducting materials, with band gap of 3.27 eV and a large exciton binding energy of 60 meV, which is twice larger than that of GaN (28 meV) [1]. Due to its extra-ordinary properties, there has been growing interest on this material for many potential applications, such as, electro-optics, spintronics, UV- LED's and sensors. In other words, the synthesis method signifies the properties of ZnO, which can be improved further by selecting suitable method. There are various methods reported to synthesize ZnO nanomaterials such as, sol–gel [2], hydrothermal [3], solvothermal [4], solid state [5], precipitation [6], solution combustion technique (SCT) [7], etc. Among all these conventional synthesis methods, the SCT is observed to be a unique method to synthesize nanocrystalline materials in as-synthesized form with large surface area at low synthesis temperatures without further need of heat treatment [8,9]. Nanocrystalline oxides are produced through the redox reaction between an oxidizer and a fuel at a moderate low temperatures of around 350–500 °C within few minutes [7,10]. In combustion synthesis, fuel to oxidizer (F/O) ratio play a critical role either in influencing the nature of combustion reaction or flame temperature. Selection of the suitable oxidizer and the fuel and their ratio controls the exothermicity of the reaction. It is well reported that, the F/O ratio of unity is known to produce highest exothermicity with complete combustion [7–9]. An arbitrary ratio of fuel to oxidizer (F/O ≠ 1) sometimes leads to formation of intermediate phases or unreacted raw materials in the final product [11]. In addition, the SCT has greater advantages, as it produce fine, large surface area and sinter active particles by using different precursors and the fuels in as-synthesized form itself without any further heat treatment. This method has all the advantages of wet-chemical processes like homogeneity, control over stoichiometry, purity and incorporation of desired amount of impurity ions. In this regard, various fuels have been tested to synthesize nanocrystalline ZnO [12,13]. In this work, we report the synthesis of nanocrystalline ZnO powders by SCT using new, eco friendly and cost effective organic fuels, which have not been used and tested to synthesize ZnO by SCT and the effect of fuel and fuel to oxidizer combinations on the properties of the final product has been studied. The structure, morphology and the properties of the resulting powders were investigated and discussed with regard to the new fuels used by establishing correlation between adiabatic temperature (T_{ad}), obtained from thermodynamic theoretical calculations, and characteristics of resulting powders.

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2. Experimental

2.1. Synthesis

Nanocrystalline ZnO particles were prepared by the SCT using Zinc Nitrate Hexa-hydrate (ZN) as an oxidizer and L-Valine, L-Glutamine and Leucine as fuels. The stoichiometric balanced equations used for the synthesis of ZnO as follows.

ZN:L-Valine

$$\mathrm{Zn(NO_3)_2\cdot 6H_2O}+\left(\frac{10\Phi}{27}\right)\mathrm{C_5H_{11}NO_2}+\left(\frac{135\Phi}{54}-\frac{5}{2}\right)\mathrm{O_2}\rightarrow \mathrm{ZnO}+\left(\frac{50\Phi}{27}\right)\mathrm{CO_2}\uparrow+\left(1+\frac{5\Phi}{27}\right)\mathrm{N_2}\uparrow+\left(6+\frac{55\Phi}{27}\right)\mathrm{H_2O}\uparrow \quad (1)$$

$(7+4.074\Phi$ moles gases produced$)$

ZN:L-Glutamine

$$\mathrm{Zn(NO_3)_2\cdot 6H_2}+\left(\frac{10\Phi}{24}\right)\mathrm{C_5H_{10}N_2O_3}+\left(\frac{60\Phi}{24}-\frac{5}{2}\right)\mathrm{O_2}\rightarrow \mathrm{ZnO}+\left(\frac{50\Phi}{24}\right)\mathrm{CO_2}\uparrow+\left(1+\frac{10\Phi}{24}\right)\mathrm{N_2}\uparrow+\left(6+\frac{50\Phi}{24}\right)\mathrm{H_2O}\uparrow \quad (2)$$

$(7+4.583\Phi$ moles gases produced$)$

ZN:Leucine

$$\mathrm{Zn(NO_3)_2\cdot 6H_2O}+\left(\frac{10\Phi}{33}\right)\mathrm{C_6H_{13}NO_2}+\frac{5}{2}(\Phi-1)\mathrm{O_2}\rightarrow \mathrm{ZnO}+\left(\frac{60\Phi}{33}\right)\mathrm{CO_2}\uparrow+\left(1+\frac{5\Phi}{33}\right)\mathrm{N_2}\uparrow+\left(6+\frac{65\Phi}{33}\right)\mathrm{H_2O}\uparrow \quad (3)$$

$(7+3.94\Phi$ moles gases produced$)$

where Φ is fuel to oxidizer (F/O) ratio.

The synthesis procedure of SCT as follows. Stoichiometric amounts of oxidizer (O) and fuel (F) were taken based on the condition that the valance of F/O to be unity, using total oxidizing and reducing valences of the oxidizer and the fuel. These stoichiometric amounts of starting materials were dissolved in double distilled water and stirred thoroughly to get transparent solution. The transparent solution was then dried on a muffle furnace at 100 °C to remove water content in the solution. So obtained sticky gel (water free) was then placed inside a pre-heated muffle furnace at 400 °C for the combustion process. Within a short duration (<5 min), the gel auto ignites with flame and with the rapid evolution of enormous amounts of gases to produce voluminous foamy product (ash). The final foamy product was collected and ground using agate pestle and mortar. The F/O ratio (Φ) was varied as Φ = 0.7 (Fuel Lean), 1.0 (Stoichiometric), 2.0 (Fuel Rich) to synthesize ZnO nanoparticles.

2.2. Characterization

As-synthesized ZnO powders were characterized through X-Ray Diffraction (XRD) (D8 ADVANCE (Bruker), operated at 40 kV/40 A using Cu Kα radiation (1.5418 Å)) for the phase confirmation. The Rietveld refinement was carried out on the XRD data to determine the structural parameters such as lattice parameters. Further, to understand the nature of combustion process in terms of the decomposition processes and the mass loss of the starting precursors (with Φ = 1) TG-DTA (NETZSCH STA 449F3) studies were carried out in a synthetic air atmosphere (80% N_2 and 20% O_2) with a flow rate of 80 mL min^{-1} N_2 and 20 mL min^{-1} O_2 in the temperature range of 25–1000 °C at a heating rate of 10 °C/min. The detailed micro-structural and structural studies were carried out for the as-synthesized ZnO samples prepared with Φ = 1, through High Resolution Transmission Electron Microscopy (HR-TEM) using LIBRA 200 TEM (M/s Carl Zeiss, Germany).

3. Results and discussion

3.1. Thermodynamic calculation

Solution combustion technique (SCT) is a well known conventional method to synthesize metal oxide nanoparticles. SCT is also known as self propagating high temperature synthesis, as the heat required to form nanoparticles is not supplied by an external source, rather it is self-generated during the exothermic reactions between the fuel and an oxidizer. The combustion reaction takes place within a short duration of time, involves rapid heating of the precursor mixture containing oxidizer and fuel with the release of enormous amounts of heat. Considering the complete combustion with no heat loss/dissipation in any form due to the short duration (~few seconds) of the exothermic reaction/combustion flaming, the combustion reaction temperature equals to be adiabatic temperature (T_{ad}). To understand and account for the heat generated by the precursor during combustion flaming, the adiabatic flame temperature is estimated theoretically for different F/O ratio using the available thermodynamic data as given in Table 1 [13–15]. Assuming the complete combustion would take place for the above stoichiometric Eqs. (1)–(3), the T_{ad} is calculated using the equation;

$$\Delta H^{o}=-\int_{T_0}^{T_{ad}}(\Sigma n\cdot C_p)_{products}dT \quad (4)$$

where 'C_p' is the heat capacity of reaction products at constant pressure in kJ/mol K, 'n' is the number of the moles, T_{ad} is the adiabatic temperature in K and ΔH^{o} is the standard enthalpy of reaction in kJ/mol.

ΔH^{o} can be calculated using the formula;

$$\Delta H^{o}=(\Sigma n\cdot \Delta H_f^{o})_{Products}-(\Sigma n\cdot \Delta H_f^{o})_{Reactants} \quad (5)$$

where ΔH_f^{o} is the standard enthalpy of formation in kJ/mol.

The results obtained from the theoretical calculations, i.e. the obtained T_{ad} and ΔH° values for different fuels and F/O ratio's are tabulated in Table 2. It is observed that, T_{ad}, ΔH° and the amount of gases evolved are varying linearly with F/O ratio.

3.2. XRD

The as-synthesized ZnO powders were characterized through powder XRD technique. The XRD patterns of the as-synthesized ZnO powders using different fuels and for various F/O ratios are depicted in Fig. 1. It is seen from Fig. 1 that, all F/O combinations

Table 1
The values of standard enthalpy of formation (ΔH_f^{o}) and heat capacity (C_p) used to calculate adiabatic temperature (T_{ad}) [13–15].

Sl. No.	Compound[a]	ΔH_f^{o}/ (kJ/mol)	C_p/(J/mol/K)
1	Zinc nitrate hexahydrate $(ZnO(NO_3)_2\cdot 6H_2O)_{(c)}$	−2305.0	–
2	L-Glutamine $C_5H_{10}N_2O_{3(c)}$	−826.4	–
3	L-Valine $C_5H_{11}NO_{2(c)}$	−628.9	–
4	Leucine $C_6H_{13}NO_{2(c)}$	−637.4	–
5	$ZnO_{(c)}$	−350.46	$45.338+7.289\times10^{-3}$ T
6	$CO_{2(g)}$	−393.51	$51.128+4.368\times10^{-3}$ T
7	$H_2O_{(g)}$	−241.83	$45.338+7.841\times10^{-3}$ T
8	$N_{2(g)}$	0	$45.338+2.544\times10^{-3}$ T
9	$O_{2(g)}$	0	–

[a] (c): crystalline, (g): gas.