O U R N A L O F

Ceramic Processing Research

Glucose as a low flame temperature fuel for synthesis of ZnO : Co nanopigments

Soudabeh Jamshidi^a, Sousan Rasouli^{b,*}, Behzad Janipour^a and Bahman Mirhadi^a

^aDepartment of Material Engineering, Faculty of Material and Engineering, Imam Khomeini International University, Qazvin, Iran ^bDepartment of Nanomaterials and Nanocoatings, Institute for Color Science and technology (ICST) 55 Vafamanesh Ave., HosseinAbad Square, Pasdaran St, 1668814811, Tehran, Iran

Nano-size ceramic powders $Zn_{0.9}Co_{0.1}O$ as green pigments have been prepared following a nonpolluting, low temperature, and self-sustaining glucose single-fuel combustion synthesis. As-prepared powders were characterized by XRD, FTIR, STA, SEM, TEM-EDX and spectrophotometer. The XRD data confirm that combustion reaction by different fuel ratio resulted in the formation of wurtzite ZnO. Scherer's equation demonstrated that the crystallite size change with five different fuel ratio (31-45 nm). SEM images illustrated that the morphology of the powder depends on the F/O ratios and changes from Semispherical to irregular particles. TEM investigation performed on powder resulted of combustion in stoichiometric fuel ratio show the formation of irregular and isolated plate-like particle. Colorimetric results also indicated a broad reflectance band around 520 nm (green region) for all samples. The observation of green appearance of different samples synthesized using different fuel/oxidizer ratios was rely on deletion of Cobalt oxide X-ray diffraction patterns and entrance of Co into ZnO structure.

Key words: green pigments, Low-temperature combustion synthesis, Glucose, Nonpolluting chemistry, Nanopowder.

Introduction

Zinc oxide (Zinc white) is used as an inorganic pigment, and when it is doped with a few per cent of cobalt atoms, a green colored solid solution would be produced. It's important to be considered that the chromium oxide based compounds are mainly utilized to generate green colors. In chromium contain pigmenting systems, oxidation of Cr(III) ion to Cr(VI) ion have negative environmental impact, since it will be segregated to the washing waters [1]. Cr(VI) is being transferred into the body through several path way such as respiratory system (the handling of Cr(VI) precursors by workers) and water or food (due to irrigation with polluted water). It can cause acute gastroenteritis, allergic dermatitis, chronic conjunctivitis, rhinopharyngitis and lung cancer. The optimum quantity of chromium (VI) compound which recommended by National Institute of Occupational Health and Safety, should not be handled over 1 mg/m3 during 10 working hours a day [2].

Thus, a factor to be kept in mind is found the substitutes for chromium (III) pigments. ZnO:Co green pigments, have demonstrated physicochemical properties that is comparable with chromium (III) green pigments. Cobalt green pigments are ecological friendly coloured pigments therefore they can be used as substitutes for chromium (III) toxic and environmentally restricted pigments [3]. On the other

hand, recently discovered that ZnO: Co green pigment is dilute magnetic semiconductors (DMS) and has special magnetic properties that could lead to a breakthrough in the field of spintronics. It can be used at room temperature, whereas other materials must be super cooled [3-7]. In the past decade, nanopigments have sparked worldwide interest due to their high surface area, which assures higher surface coverage, more intense colors, higher number reectance points and hence improved scattering in comparison with those of their bulk counterparts [8]. Of the most accessible, rapid, and economic soft methods for the synthesis of various nanocrystalline oxides which afford highly crystalline and pure materials is considered to be Solution Combustion Synthesis (SCS). The redox reaction between an oxidant (O, usually the nitrate anion) and a fuel (F, an organic molecule which ignites the reaction) which thermally generated, is self sustained, uses relatively simple equipments and generally low cost reactants [9]. The ame temperature and the entire combustion process and ultimately the structural characteristics of metal oxides are critically influenced by the thermochemical characteristics of fuels. In modern combustion synthesis the involvement of less polluting and low-temperature ame fuels represent a new trend as an advantage in the synthesis of homogeneous nanocrystalline oxides [10].

Glucose is a monosaccharide (or simple sugar) that is a very important carbohydrate in biology. Its natural origin fullls modern ecological requirements (highly available, non-toxic, renewable, low cost, and biodegradable), while its large heat of formation has recommended it to be classified in low-temperature ame fuels. Despite, the carbohydrate existence usually

^{*}Corresponding author:

Tel : +98-21229-52272

Fax: +98-21229-47537

E-mail: rasouli@icrc.ac.ir

along with a high-temperature fuel (e.g. urea, glycine) in order to decrease the reaction exothermicity [11, 12]. Though several positive effects are expected in a singlefuel glucose-assisted combustion reaction: generates a no explosive combustion process and produces nontoxic gases (mostly CO2 and H2O), so can be classified in safe fuels related to combustion reaction. Sulcova and Torjan [3] reported the synthesis of pi ZnO: Co pigment. Considering results, an intense green hue can be obtained by $Zn_{0.9}Co_{0.1}O$ compared to other compositions of. ZnO: Co. We present the synthesis and characterization of cobalt green pigment, formulated as $Zn_{0.9}Co_{0.1}O$ following a combustion reaction which uses glucose as singlefuel.

Experimental Procedures

Synthesis

The exothermic redox stoichiometric reactions between oxidizer and fuel to achieve $Zn_{0.9}Co_{0.1}O$ solid solution can be expressed as follows:

$$0.9n(NO_3)_2 \cdot 6H_2O + 0.1Co(NO_3)_2 \cdot 6H_2O + \Psi C_6H_{12}O_6$$

 $Zn_{0.9}CO_{0.1}O + 6\Psi CO_2 + (6 + 6\Psi)H_2O + N_2$

The molar ratios of oxidants-to-fuel (F/O), denoted as Ψ . Here, the F/O ratio remains stoichiometric of 10/24, which means that all oxygen required for fuel combustion derives from the oxidant.

All reagents were of analytical grade and used as received without further purifications. In a typical synthesis, $Zn(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, glucose $(C_6H_{12}O_6)$, were mixed in the required molar ratios in a minimum volume of deionized water to obtain transparent aqueous solutions. These solutions after thermal dehydration (at ≈ 80 °C on a hot plate to remove the excess solvent) gave highly viscous liquids. As soon as the viscous liquids were formed, then, the beaker vessel was transferred into microwave oven (Samsung, Korea, 900W, 2.45 GHz frequency) to complete the combustion reaction after about 50 s. At this stage, the viscous liquid swelled and auto-ignited, with the rapid evolution of large volume of gases, to produce voluminous green powders.

Characterization

The obtained green powders were characterized by X-ray diffraction using a D-500 (Siemens, Karlsruhe, Germany) diffract meter. Thermal measurements were performed on a Perkin Elmer (Pyris Diamond / *DTA*) and morphology of the samples were observed by LEO 1455VP scanning electron microscope (SEM) and transition electron microscopy (TEM). The elemental distribution of samples was determined with an attached energy dispersion X-ray spectrometer (EDX, Oxford Instruments).Color properties of the obtained products were determined by Ultraviolet radiation

spectroscopy in the visible-ultraviolet light region. Diffuse reectance was determined with a Color Eye 7000A spectrometer in the range between300 and 700 nm.

Results and Discussion

In typical procedure, we use glucose as a fuel and complexing agent and zinc and cobalt nitrate hexahydrate as an oxidant. The powder characteristics are mostly regulated by heat of combustion and gas evolution, which themselves are dependent on nature of the fuel and oxidant-to-fuel ratio. Five different molar ratios of oxidants-to-fuel were chosen for Zn_{0.9}CO_{0.1}O nano pigment. The stoichiometric ratio (1Ψ) , two samples are fuel-deficient ratio (0.25Ψ) and 0.5Ψ) and two sample are fuel-excess ratio (1.5 Ψ and 2Ψ). The samples have been prepared by the aforementioned F/O were termed ZC1G, ZC2G, ZC3G, ZC4G and ZC5G, respectively. The generation of heat of combustion and gas evolution are two general steps which occur during the combustion process. The crystallization and formation of the desired phase are specifically affected by Heat of combustion (or flame temperature). Although, powder characteristics can be adversely affected by a very high flame temperature during the reaction which can lead to the increase in the crystallite size, fabrication of hard agglomerates and thereby specific surface area reduction, so the sinter ability declines [13]. Here is the chemical reaction for the standard enthalpy of glucose:

It is well known that the standard enthalpy of formation for glucose can be expressed as [14]:

$$\Delta H^{o}_{com,glucose} = [6 \times \Delta H^{o}_{f,CO2(g)} + 6 \times \Delta H^{o}_{f,H2O(g)}] - [\Delta H^{o}_{f,glucose} + 6 \times \Delta H^{o}_{f,O2(g)}]$$
(1)

Using the thermodynamic data for reactants and product and the enthalpy of reaction for Eq. (1), the heat of formation glucose can be determined as follows:

$$\Delta H^{o}_{f,glucose} = -1268.2(kJ.mol^{-1})$$

Large heat formation of glucose $(-1268.2 \text{ kJ.mol}^{-1})$ Causes to be reduces flame temperature which it's prevents the agglomeration of the particles and hinders the grain growth. So molecules decomposes occur at much lower temperature (< 200 °C). For this reasons large volume of gases, can be rapidly evaluated during the glucose molecule decomposition which releases the heat of combustion quickly from the system by



Fig. 1. STA curves of the gel obtained quenching befor being ingited in nitrogen atmosphere at a heating of $10 \, {}^{\circ}\text{C}$ /min.

convection and limits the rise of temperature, thus reducing the possibility of premature local partial sintering among the primary particles and it is recommended as low temperature flame fuel.

Thermal analysis

To well understand the combustion process, we fulfilled Simultaneous Thermal Analysis (STA) investigations in nitrogen atmosphere at a heating rate of 10 °C /min to characterize the gel obtained by quenching before igniting in the amount of stoichiometrical F/O ratio. As exhibited in Figure 1. The decompositions start with the endothermic dehydrations (43.1-91.3 °C, 13% weight loss). Two adjacent exothermic peaks appeared in 106 and 133 °C accompanied by an abrupt loss in weight (84-120 °C / 130-140 °C, 27 / 35% weight loss) which are attributed to the combustion reaction of the gel. The ignition temperature is specified by the decomposition temperature of one of the reagents in the solution (oxidant or/and fuel). In these systems, the exothermic peak is close to the decomposition temperature of zinc nitrate hexahydrate (105-131 °C) [15] and is lower than the decomposition temperature of glucose (170.3 °C) [16]. The nitrate decomposition continues as the temperature is rising and causes the breakdown of the glucose structure. The endothermic peak in 435 °C was due to elimination of the residual nitrate in sample. In solution combustion reaction the driving force originated from internal chemical energy, whicWh is from the highly exothermic redox reaction. The initial energy consumption is just used for dehydration of the precursor solution, and the required temperature can be described as that for the reaction initiation. Hence, the temperature required in solution combustion reaction is slightly higher than the ignition temperature (135 °C in the present case), making the synthesis route energy-saving.

Crystal structures of the synthesized samples

The phase composition of the products derived using different molar ratios of oxidants-to-fuel were recognized from the XRD patterns recorded after combustion (in Figures 2). The main phase characterized in all the patterns indicates the formation of pure ZnO phases, correspond to



Fig. 2. XRD patterns of powder Zn-CoO pigments synthesized by combustion method.

hexagonal wurtzite (W) structure, that can be indexed by comparison with data from JCPDS file no. 00-079-0207 and space group P63mc with lattice constants $a = 3.2568 A^{\circ}$, $b = 3.2568 A^{\circ}$, and $c = 5.2125 A^{\circ}$. As the patterns show, crystallite ZnO phase is relatively insensitive to F/O variations. Even high fuel lean combustion ZC1G has led to appropriate ZnO phase formation. However, some weak peaks are appeared that belong to Co₃O₄ with Fd-3 m structure (ICDD 01-080-1540) in the ZC1G sample. The formation of cobalt oxide in the ZC1G combustion sample can be correlated to low-energy combustion process. Presence of CoO with Fd-3 m structure (ICDD 01-071-1178) that identified in ZC5G sample, it can be explained that when the fuel ratio is 2 times greater than stoichiometric state, reaction rate increases, for this reason Co²⁺ cannot completely diffused into the ZnO lattice structure and generate CoO. It seems that XRD patterns corresponding to ZC2G, ZC3G and ZC4G are related to well-crystalline single phase ZnO solid solutions after combustion process without any further calcinations steps. Whereas, calcinations process is needed for the combustion synthesis performed with urea and citric acid as fuel. [17]

Herein three sample, indicating synthesis of the single phase zinc oxide as no traces of extraneous phases such as Co3O4 or other impurities are observed within the X-ray detection limit, which show that the Co ions successfully reside in the lattice site rather than interstitial ones. The absence of the XRD peak shift on doping of ZnO with Co is rational given that the ionic radii of tetrahedrally coordinated Co^{2+} and Zn^{2+} are entirely similar at 0.072 and 0.074 nm, respectively [18, 19].

The average crystallite size is determined by the relationship between crystal grain size and X-ray line broadening, described by the Scherer's equation [20]:



Fig. 3. Effect of F/O ratio on the average crystallite size of synthesized sample.

$$D_{h,k,l} = 0.9 \ \lambda/\beta \ \cos\theta \tag{2}$$

Where D is the average crystallite diameter, λ is the wavelength in angstrom, β , is the half-maximum line width (FWHM) and θ is the Bragg angle D for the three different molar ratios of oxidants-to-fuel obtained is given in Fig. 2. The decrease of flame temperature in ZC1G (0.25Ψ) can be effectively preventing nanocrystallites from sintering and decrease average crystallite size. As the figure shows, the crystallite size from ZC1G to ZC2G raised. At this state from 0.5Ψ -1 Ψ ratio increasing has no effect on crystallite size. With increase F/O ratio to 1.5 decline crystallite size which can be due to releasing higher volume of gaseous molecules that removes more heat from the system by convection and further lowers the flame temperature. While F/O ratio increases to 2Ψ amount again the crystallite no changed.

Chemical and structural changes, which occur during combustion can be monitored by the Fourier transform infrared (FTIR) in KBr matrix. Figure 4 shows the spectra of the as-synthesized powders (five F/O ratios) in the range of 450-4000 cm⁻¹. The peaks of bonds metal-oxygen, observed at absorption peak fewer than 650 cm⁻¹, indentified peaks around 540 cm⁻¹ attributed



Fig. 4. FTIR spectrums of $Zn_{0.9}Co_{0.1}O$ powders obtain combustion synthesized.

to the asymmetric stretching mode of the tetrahedral ZnO_4 group present in the wurtzite ZnO structure. The absorption peak at 1600 cm⁻¹ from the FTIR spectrum was due to carboxyl group. Absorption peaks around 1400-900 cm⁻¹ indicating No³⁻ ion and the broadening bands that disappeared at 3700 and 2700 cm⁻¹ corresponding to the vibration mode of water O-H group indicate the presence of a small amount of water adsorbed on the ZnO nano-crystal surface. This is consistent with results reported previously [18, 21, 22]. According to FTIR spectrum, the remained Nitrate ratio in ZC1G sample is further than other samples. The Reason for this is the uncompleted accomplishment of the redox reaction.

The microstructures of synthesized samples

Fig. 3 shows the microstructures of as-synthesized Zn-CoO powders with different molar ratios of oxidants-to-fuel. From this images, it seems that, for ZC1G and ZC2G powders consists of semispherical loosely agglomerated particles may be due to the low amount heat of formation (figure3 (a) and (b)). When in the presence of metal nitrate-fuel combustion starts, the heat localization on the particle boundaries results in



Fig. 5. SEM image for five different molar ratios of oxidants-to-fuel (a) ZC1G (0.25 Ψ), (b) ZC2G (0.5 Ψ), (c) ZC3G (1 Ψ), (d) ZC4G (1.5 Ψ), (e) ZC5G (2 Ψ).



Fig. 6. (a) TEM image, (b) SEAD pattern, and (c) EDX spectrum of the Zn0.9Co0.1O powder resulted stoichiometric ratio.

semi-sintered particles [25rasuli AG = 23] observed in Figure 3 (c). Furthermore, heighten of localized heat with increases glucose content leads to rapid crystal growth. The increase of particle size in fig3(c) in comparison with fig. 3(a) and 3(b) is in good agreement with the results of the crystallite size is shown in Figure 2. In the case of fuel-excess ratio (ZC4G), the larger amount of gaseous products, which fragment the product while escaping, to give the crystallites scatter in all directions and finer particles (figure 3 (d)). While F/O ratio increases to the Double amount of stoichiometrically state (ZC5G), the sinterability tendency has increased to form the partially sintered agglomerates as show in figure 3 (e). This tendency is due to an increase in surface area and surface energy, which is a driving force for sintering during combustion process. [24].

Figure 3a, shows TEM investigation performed on the $Zn_{0.9}Co_{0.1}O$ powder resulted stoichiometric ratio, and consists of irregular and isolated particles, showing a signi?cantly low agglomeration propensity with platelike morphology. Particle size approximations were calculated using the ImageJ software package. A rather bimodal particle size distribution, where smaller (*26.25 nm) and single crystal particles coexist with larger (*57.66 nm), and the overall mean particle size estimated from Fig. 4a is of 45.02 nm.

The higher crystallinity degree of the $Zn_{0.9}Co_{0.1}O$ particles is pointed out by the well-marked fringes in the SAED pattern (Fig. 3b) by the obviously larger and brighter spots composing the diffraction rings in the SAED pattern. Qualitative (Figs. 3c) and quantitative EDX profiling have demonstrate the uniformity of elemental composition of the Co-doped ZnO with Zn, Co and O peaks consistent and high purity, as well as the suitable stoichiometry of the investigated $Zn_{0.9}Co_{0.1}O$ powders.

Color properties of synthesized samples

The color properties of the products derived using different molar ratios of oxidants-to-fuel have been determined by the CIELAB coordinates and spectral re?ectance. As Fig.7 shows, the color properties in the CIEL* a^*b^* and the CIE $L^*c^*h^\circ$ color spaces are applied.

In color space of CIE $L^*a^*b^{**}$, L^* indicate the lightness axis (where black is equal to 0 and white to 100), b* represents the color difference between blue



Fig. 7. CIE $L^* a^* b^{**}$ and CIE $L^* c^* h^0$ color systems.

(negative axis) and yellow (positive axis), a* shows the color difference between green (negative axis) and red (positive axis). In a polar coordinate system, i.e. CIE $L^*c^*h^o$, c* indicates the chroma axis whit a minimum value equal to zero for an achromatic shade and h° is the hue angel varying from 0 to 360 while angles of zero, 90, 180, 270 and 360 represent red, yellow, green, blue and red hue, respectively [25]. C* and h is de?ned as follows [18]:

$$C^*_{ab} = \{(a^*)2 + (b^*)^2\}^{1/2}$$

 $h^o_{ab} = \tan^{-1}(b^*/a^*)$

Figure.8 indicates the diffuse re?ectance spectra of the pigments. In accordance with the results Figure.8, for all samples, obtained a similar hue whit a shade accord in green region of the visible spectrum whit the maximum reflection around 520 nm. Figure 8 demonstrate which the curves differ mainly in terms of brightness. Though the very poor absorption for Sample ZC1G and ZC5G meaning a grayish green shade. In addition, the tristimulus values of the samples are listed in Table 1. An intensive color is defined as a poor or rich shade and should be determined by c* values. Cunha *et al.* [19 = 26] Illustrated that saturated green color of? Zn_{0.9}Co_{0.1}O pigment been obtained only for a complete entrance of Cobalt into ZnO structure.

Except for samples ZC1G and ZC5G which shows a

Table 1. Colorimetric data of Zn0.9Co0.1 O powders prepared by combustion in the presence of different Ψ content.

sample	L^*	<i>a</i> *	<i>b</i> *	с*	h°
ZC1G	30.53	-0.90	0.72	1.15	141.18
ZC2G	45	-22.18	5.33	22.81	166.49
ZC3G	46.3	-23.12	5.54	23.77	166.53
ZC4G	36.66	-17.93	0.74	17.95	177.65
ZC5G	38.76	-6.84	-0.02	6.84	180.20



Fig. 8. The diffuse reflectance spectra of the samples synthesized using different fuel ratio.

minimum c* equal to 1.15 and 6.84 respectively, and shows poor green shade, the other sample have high value of c* are green shade. Low value of c* in ZC1G and ZC5G sample, assigned to have not been entered cobalt in ZnO structure that it confirmed with results of XRD analyse, and reveal cobalt in form of cobalt oxide. This confirms that different color properties were achieved, which can be well attributed to the crystal structure, powder morphology and the state of particles agglomeration depending on fuel content.

Conclusions

In this paper, we show a fast and nonpolluting method for producing nanoscale ceramic powders $Zn_{0.9}Co_{0.1}O$ as ecological friendly green pigments based on combustion reactions, in which glucose was used successfully as low-temperatures single-fuel. The structural data confirm the presence of wurtzite phases for all samples, at relatively low temperatures, and confirming the efficiency of the proposed procedure. Fourier transform infrared spectroscopy confirmed the formation ZnO4 band after the combustion reaction in all samples. The morphology of synthesized powders change as a function of fuel ratio. TEM investigations for stoichiometric samples revealed polycrystalline nature, which each particle is remarked a plate-like morphology and lower tendency to agglomerate.

Deeper green color with respect to higher C*, h and intense green reflectance (520 nm) was obtained by ZC3G and ZC2G samples. The method recommended here depicts a successful start to expand the very selective family of fuels with natural, different, and less-polluting members, namely the carbohydrates.

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