

Effect of citric acid composition on the citrate-nitrate auto-combustion synthesis of ZnO nanoparticles

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ABSTRACT – In this work, the citrate-nitrate auto-combustion reaction has been developed as a new route in synthesizing ZnO nanoparticles. The decomposition characteristics of ZnO precursor gels are investigated in regard to citric acid compositions. Via this method, the aqueous Zn nitrate ($Zn(NO_3)_2$) was mixed with a calculated amount of citric acid to obtain a series of the mixture solution with citric to nitrate ratio, c/n from = 0.3, 0.4, 0.5, 0.6 and 0.7. The pH of the mixture was adjusted to $pH \approx 7$ by adding liquor ammonia and was heated at 250 °C on the hotplate with an infrared lamp at the top. During the drying process, the solution changed to the gel form before automatically combusted and transformed into fine ashes. The TG/DT analysis of the gel samples indicate that the Zn nitrate decomposed in a single step highly exothermic reaction at around 240 °C in samples with $c/n \leq 0.6$. While the sample with $c/n = 0.7$ decomposed with double-step reactions at 240 °C and 300 °C.

1. INTRODUCTION

The scientific community has witnessed a rapid revive and expands of the ZnO due to its fascinating electrical and optical properties. The ZnO in form of hexagonal wurtzite crystal structure is widely known to exhibit high direct band gap of 3.3 eV, high optical gain, high electrical conductivity, the high optical transmittance in a visible region, and large binding energy [1]. Nevertheless, various forms of ZnO have been synthesized, but then again the ZnO nanoparticles attracted much attention due to quantum confinement of nanoparticles which would bring to novel properties. In spite of the rapid developments, controlling purity and structural stabilities of ZnO nanoparticles have remained a major challenge. Javed et al. [2] stated that ZnO nanoparticles are stable but instability happened when the agglomeration of poorly distributed nanoparticles due to high surface energy results in size increase. Therefore in order to obtain highly pure and well-distributed ZnO nanoparticles, the selection of synthesis method is crucial. One appealing method is the citrate-nitrate auto-combustion reaction which has been reported was used in synthesizing highly pure oxides nanoparticles include Al_2O_3 , $YBa_2Cu_3O_{7-\delta}$, and ZrO_2 with good particles dispersion and better control of compound compositions [3]. The high-temperature combustion process can vaporize all impurities while the calcination process afterward provides thermal and structural stability to the powder. Thus in this work,

citric acid is used as the oxidizing agent or fuel to the combustion reaction where the Zn nitrate is oxidized to ZnO. The composition of citric acid is controlled while its effect towards the combustion characteristics is investigated.

2. METHODOLOGY

The aqueous solution of $Zn(NO_3)_2$ (0.5 M) was prepared by dissolving $Zn(NO_3)_2$ reagent powders (99.9 % pure) in distilled water. The calculated amount of aqueous citric acid (0.5 M) was mixed with the $Zn(NO_3)_2$ solution to achieve mixtures with the citric-nitrate ratio, c/n from 0.3 to 0.9. The pH of the mixture was adjusted to $pH \approx 7$ by adding liquor ammonia before dried on the hot plate at 250 °C. Infrared lamp has been used to provide uniform heating from on top of the mixture. Drying process was continued until the mixture solution turned into the gel and combusted into ashes. A portion of the gel was taken for thermal analysis. Thermal decomposition of the precursor gels was characterized by thermal gravimetric (TG) and differential thermal analysis (DTA). These studies were performed under Argon atmosphere from room temperature to 800 °C by a heating rate of 5 °C min^{-1} in a NETZSCH thermal analyzer unit (409C) and using α -alumina as a reference for DTA.

3. RESULTS AND DISCUSSIONS

The TG-DTA curves of the gel samples are shown in Figure 1. Generally, each gel lost its mass with relatively the same pattern as can be seen from the TG curves, started with minor lost at the temperature 100 °C - 200 °C, followed by a major drop at temperature 200 – 250 °C and constantly reduced plateau until 800 °C. In the same figure, the exothermic peak of DTA curves shows the main auto-combustion reaction of the gel samples which had occurred at temperatures in the range of 220 °C to 232 °C. Detail observation on TGA and DTA curves in Figure 1 revealed that the gel samples decomposed in three different behaviors. The first behavior is fast decomposition shown by the gel samples with $c/n = 0.3$ and 0.4. The gels lost about 40 % and 10 % of its mass at around 220 °C and 390 °C respectively. The DTA curves of these gels show fluctuations of exothermic and endothermic peaks during the main decomposition attributed to the non-flammable reaction. The second behavior is rapid decomposition where the gel samples with $c/n = 0.5$ and 0.6 were rapidly lost around 45 % of its mass in a single

reaction at a temperature around 230 °C. The DTA curves of these gels showed a single highly intense exothermic peak which indicated that the gel undergoes flammable combustion. While the third behavior is slow decomposition or repeated decomposition which occurred to the gel samples with $c/n = 0.7$. During this decomposition, the gel slowly lost its mass several times due to the repeated combustion reaction indicated by many exothermic peaks of DTA curves. A thermally stable plateau is formed on TG curve at the end of each type of decomposition behavior.

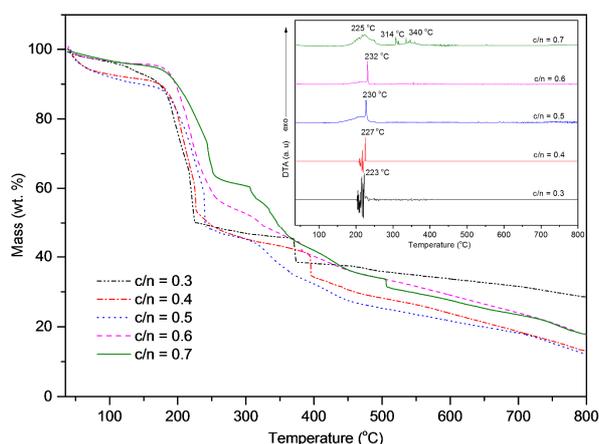
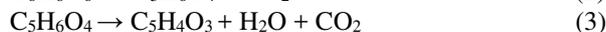


Figure 1. TGA curve of the gel samples with different c/n ratio. Inset shows DTA pattern of the samples.

The minor loss of mass at around 100 °C to 200 °C is due to the removal of excesses water and decomposition of citric acid. As the temperature increases, citric acid ($C_6H_8O_7$) began to decompose to aconitic acid ($C_6H_6O_6$) at the temperature 183 °C by the reaction shown in Equation (1) [4]. Upon heating, aconitic acid is further decomposed to itaconic acid ($C_5H_6O_4$) as shown in Equation (2). Polymerization reaction for itaconic acid has occurred when reached its melting temperature of 166 °C which produced itaconic anhydride ($C_5H_4O_3$) with byproduct water (H_2O) and carbon dioxide (CO_2) shown in Equation (3). The itaconic acid will be acted as a fuel once ignited.



The overall decomposition reaction that involved zinc nitrate and citric acid is shown in Equation (4).



In this redox reaction, the citrate ion is acted as the reducing agent while nitrate ion acted as the oxidizing agent. The combustion process is done within a few seconds and emitted a large amount of carbon dioxide (CO_2) and nitrogen (N_2) gases. This kind of combustion mode is found in the rapid decomposition combustion for sample $c/n = 0.5$ and 0.6 . While in the fast decomposition, gels with $c/n = 0.3$ and 0.4 which had

less citric acid composition hence less itaconic acid were dehydrated before the main combustion can occur as suggested by the fluctuations of endothermic and exothermic reactions phenomenon. Whereas the second mass loss can be attributed to the decomposition of volatile matters such as itaconic anhydride at around 390 °C. For the slow or repeated decomposition combustion in the sample, c/n ratio = 0.7 are due the excessive amount of citric acid added. Initially, the gel is ignited at the temperature around 230 °C, both itaconic acid and zinc nitrate are decomposed to itaconic anhydride and zinc oxide respectively. Hence, it can be observed that there is major mass dropped. Throughout the combustion process, there is a large amount of itaconic acid is not fully decomposed due to the excessive citric acid and the difference in temperature gradient [4]. However, the second decomposition of aconitic acid takes place at the temperature range of 370 °C to 450 °C. The aconitic acid is completely decomposed and converted to itaconic acid and emitted a large amount of heat energy. The temperature dependence reactions during the combustion reaction can be summarized in Table 1.

Table 1. Decomposition reaction of the gel samples at specified temperature.

Sample (c/n)	Reaction at the specified temperature		
	30-200 °C	200-300 °C	300-400 °C
0.3	Dehydration of gel	Combustion	Removal of volatile matters, and trapped air.
0.4	Dehydration of gel	Combustion	
0.5	Dehydration of gel	Flammable combustion	Formation of intermediate ashes containing ZnO.
0.6	Dehydration of gel	Flammable combustion	
0.7	Dehydration of gel	Slow decomposition	Second combustion of $c/n = 0.7$ gel.

4. CONCLUSION

The auto-combustion reaction of the ZnO nanoparticles precursor gel is optimized by using citric acid with the composition; 0.5 and 0.6 of c/n ratios.

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