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Hydrothermal Synthesis of Zinc Carbonate Hydroxide Nanoparticles

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Abstract

Zinc carbonate hydroxide $Zn_5(CO_3)_2(OH)_6$ nanoparticles have been successfully synthesised by the hydrothermal treatment of an aqueous solution of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and urea ($NH_2CONH_2$) at 120 °C. The as-synthesized nanoparticles were characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA). XRD and SEM revealed $Zn_5(CO_3)_2(OH)_6$ nanoparticles produced in 20-40 nm size range with spherical morphology. TGA showed the expected one-step decomposition of zinc carbonate hydroxide to zinc oxide (ZnO) between temperatures of 180 °C and 350 °C. The hydrothermal reaction time (2, 3 and 4 hours) studied did not show any significant effect on the particle size and morphology. However, the crystallinity of the synthesised nanoparticles seems to be enhanced at longer hydrothermal reaction time by showing larger XRD diffraction peaks.

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1. Introduction

There has been an increasing industrial interest in tailor-made nanoparticles due to their potential of new applications [1, 2]. Among such materials is zinc carbonate which found its way as a useful substance in different

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sectors of the industry. Zinc carbonate has been used in respirators due to its effectiveness in removing toxic gases such as SO_2 and HCN [1, 3]. One of the most important applications of zinc carbonate is its use as a precursor for the production of ultrafine zinc oxide (ZnO) which has numerous uses in the industry such as in electronics, solar cells, pigments and as an industrial catalyst [1-4].

Several zinc carbonate synthetic routes have been previously investigated. Zhang et al. (2004) synthesized zinc carbonate hydroxide ($Zn_5(CO_3)_2(OH)_6$) by direct precipitation of potassium carbonate (K_2CO_3) with zinc acetate ($Zn(CH_3COO)_2$) at room temperature [3]. Wu & Jiang (2006) synthesized pure anhydrous $ZnCO_3$ nanocrystals by a solid-state reaction [2]. The experimental method consisted of grinding zinc sulphate heptahydrate ($ZnSO_4{\cdot}7H_2O$) and ammonium bicarbonate (NH_4HCO_3) in the presence of small amounts of polyethyleneglycol-octyl-phenylate (OP) surfactant at room temperature. Shamsipur et al. (2013) synthesized basic $ZnCO_3$ nanoparticles using direct precipitation of zinc nitrate heptahydrate ($Zn(NO_3)_2{\cdot}7H_2O$) and sodium carbonate (Na_2CO_3) [1]. Hu et al. (2010) synthesized ($Zn_5(CO_3)_2(OH)_6$) by a hydrothermal reaction of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and urea ($NH_2CONH_2$) [5]. Hingorani et al. (1993) synthesized zinc carbonate as a precursor for the production on ZnO using a microemulsion technique [6]. The authors utilized a CTAB/1-butanol/n-octane/aqueous phase system with the aqueous phase comprised of either zinc nitrate ($Zn(NO_3)_2$) or ammonium carbonate ($(NH_4)_2CO_3$). One of the process challenges is to synthesise nanoparticles having homogenous size and morphology distributions.

Hydrothermal process is defined as a process, in which chemical reactions occur in aqueous or organo-aqueous media, under the simultaneous application of heat and pressure [7]. Hydrothermal processes poses several advantages over conventional nanoparticle synthetic routes such as the use of relatively lower reaction temperatures to obtain particles with reduced agglomeration, narrower particle size distributions, greater phase homogeneity and controlled particle morphology. As a result, this process has successfully been implemented in the synthesis of a wide-range of different nano-materials [7, 10-15]. In this study, the synthesis of zinc carbonate nanoparticles was carried out by utilizing a hydrothermal process for the ability to synthesis the nanoparticles with homogeneous particle size and morphology distributions. The particles were sythesised by hydrothermally treating an aqueous solution of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and urea ($NH_2CONH_2$) at 120 °C for 2, 3, and 4 hours. The crystal structure, size and morphology of the synthesised particles have been studied by XRD, SEM and TGA.

2. Experimental

2.1. Zinc carbonate synthesis

Analytical grade Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and urea ($NH_2CONH_2$) were utilized as starting material. Both reagents were purchased from Sigma-Aldrich UK and used without further purification. Deionized water was used in all experiments. The hydrothermal synthesis of $ZnCO_3$ nanoparticles was carried out by utilizing a procedure similar to that reported by Hu et al. (2010) [5]. Known quantities of the starting materials were first accurately weighed and transferred into a 250 ml conical flask. The reagents were then dissolved in 100 ml deionized water with magnetic stirring to produce a clear and homogenous solution of 0.05 mol/L zinc acetate dihydrate and 0.1 mol/L urea. 120ml of this clear solution was then transferred into a Teflon-lined stainless steel autoclave with an inner volume of 160 ml, heated in a electric oven to 120 °C and kept under isothermal conditions for the specified hydrothermal time of 2, 3 or 4 hours. After the heating process, the hydrothermal vessel was left to cool under room temperature conditions. The as-prepared samples were then filtered using a Buchner-funnel connected to a pump with filter paper 47 mm in diameter and 0.22 μm in pore size. After filtration, the samples were washed twice with deionized water and twice with absolute ethanol and then dried in an oven at 60 °C for 6-12 hours. Fig. 1 shows a systematic diagram of the hydrothermal procedure adopted for this study.

2.2. Characterization

X-ray powder diffraction (XRD) analysis was carried out on the dried powder to study the crystal phase of particles produced from the hydrothermal process at different time intervals. The Bruker AXS D8 Advance XRD setup was used and the XRD patterns of all the samples were recorded in the range of $8° \leq 2\theta \leq 75°$ with a Cu K_α source at 35 kV, 45 mA.

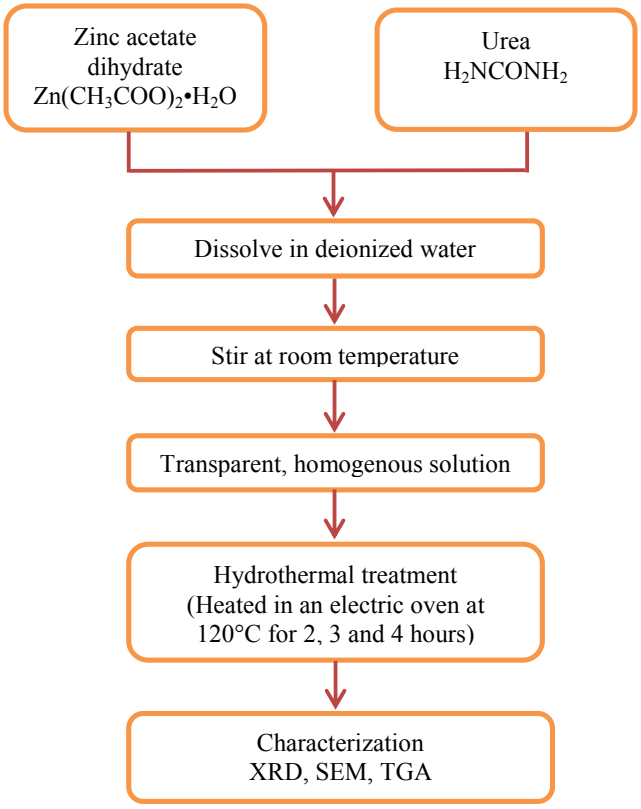

Fig. 1. Flow chart showing the experimental procedure for producing zinc carbonate nanoparticles by hydrothermal process [5].

High-resolution surface images of the obtained particles were taken using scanning electron microscopy (SEM; LEO 1530 Gemini). SEM samples were prepared by diluting the powder sample in ethanol and then drying few drops on an aluminum stub. The samples were then coated using platinum before examining them under microscope. Thermogravimetric analysis (TGA; Mettler Toledo TGA/SDTA 851°) was carried out on the dried powder in nitrogen atmosphere. The heating profile consisted of a steady increase in temperature at a rate of 10 °C/min from 30 to 480 °C, followed by maintaining isothermal conditions at 480°C for 10 minutes.

3. Results and Discussion

The XRD patterns of the hydrothermally synthesized particles at different process times are shown in Fig. 2. The obtained diffractograms were compared with the Powder Diffraction File (PDF) database provided by the International Centre for Diffraction Data (ICDD) with the help of the instrument's software (X'Pert HighScore Plus). The best matching database pattern was found to be zinc carbonate hydroxide ($Zn_5(CO_3)_2(OH)_6$) also known as hydrozincite, with card number No. 04-013-7572 (Fig 2(a)). However, some of the peaks seem to match better with reference pattern of zinc carbonate hydroxide hydrate ($Zn_4CO_3(OH)_6·H_2O$), card number No. 00-011-0287. This confirms that the particles produced are a mixture of ($Zn_5(CO_3)_2(OH)_6$) and ($Zn_4CO_3(OH)_6·H_2O$), however ($Zn_5(CO_3)_2(OH)_6$) is present in larger quantities as evident by generating higher computer peak matching score during XRD pattern indexing.

Fig. 2 (b) shows the diffraction patterns of the hydrothermally synthesized zinc carbonate nanoparticles at 120 °C for 2, 3 and 4 hours. It can be seen from Fig. 2(b) that the crystallinity of the prepared nanoparticles was enhanced with the increase in hydrothermal reaction time. The diffraction peaks obtained from the particles prepared at 2 hour hydrothermal time appear to be weak with low intensity; however, an increase in hydrothermal time to 3 and 4 hours

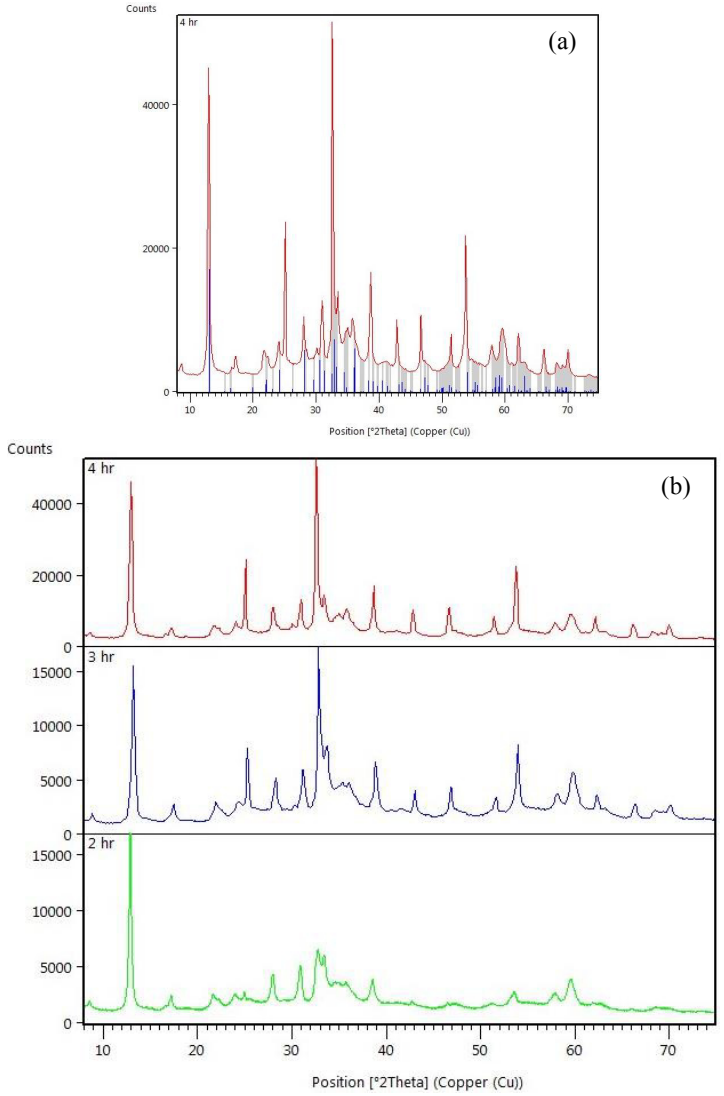

Fig.2. XRD diffraction patterns of hydrothermally synthesised zinc carbonate nanoparticles at 120 °C for 2, 3 and 4 hours.

clearly shows an increase in peaks intensity and sharpness indicating improved crystallinity of the product. The overall background of XRD patterns is also an indication of the amount of amorphous content present, which is noticed to be reduced with increasing hydrothermal treatment time, hence improved crystallinity. This agrees with the conclusion drawn by Hu et al. (2010), which states that an increase in hydrothermal time improves the formation of hydrozincite crystals [5].

Fig. 3 shows the surface morphology and particle size of the hydrothermally synthesised zinc carbonate nanoparticles by SEM. It can be seen that the individual particles generally exhibit spherical morphology with particle size ranging from 20-40 nm. However, some larger aggregates are also observed which can be associated with the interparticle interactions normally expected to be found in nano-scale particles. As for the effect of hydrothermal process time, SEM images do not show any significant correlation between hydrothermal time and the particle size and morphology distributions. Overall, we observe that the zinc carbonate particles produced hydrothermally can be classed as having homogeneous size and morphology distributions.

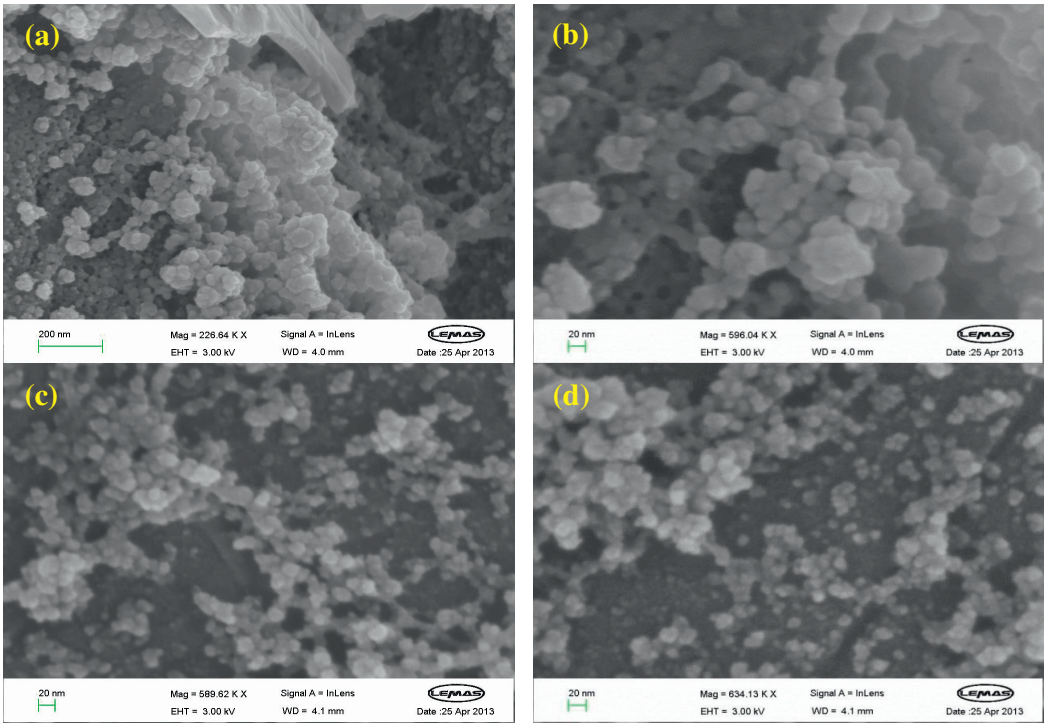

Fig.3. SEM images of the hydrothermally synthesised zinc carbonate nanoparticles at 120 °C for (a, b) 2 hours and (c, d) 3 hours.

The decomposition process of $Zn_4CO_3(OH)_6 \cdot H_2O$ and $Zn_5(CO_3)_2(OH)_6$ to form zinc oxide (ZnO) can be illustrated by reactions (1) and (2) below [4, 8, 9], with theoretical percentage mass loss of 25.2 % and 25.9 %, respectively.

$$Zn_4CO_3(OH)_6 \cdot H_2O \rightarrow 4ZnO + CO_2 + 4H_2O \quad (1)$$
$$Zn_5(CO_3)_2(OH)_6 \rightarrow 5ZnO + 2CO_2 + 3H_2O \quad (2)$$

Fig. 4 shows the TG curve obtained from the nanoparticles hydrothermally synthesised at 120 °C for 4 hours. As expected, Fig. 4 shows the typical single-step decomposition process between approximately 180 °C and 350 °C in which $Zn_5(CO_3)_2(OH)_6$ and $Zn_4CO_3(OH)_6 \cdot H_2O$ decompose to form ZnO with the release of CO_2 and H_2O. Within this single step, however there is a minor weight change event from 280 °C to 350 °C, which could possibly be due to the mixture of two phases present and change in crystal structure. The calculated percentage weight loss from Fig. 4 was 26.9 % which is comparable to the theoretically calculated value.

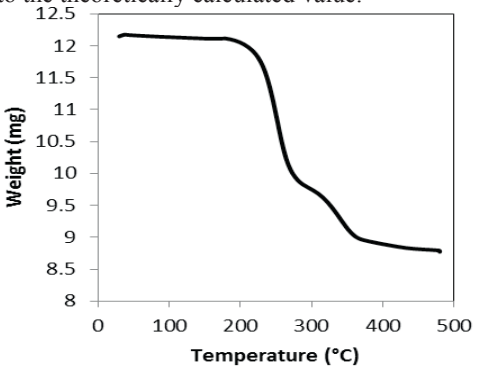

Fig. 4. TG curve of hydrothermally synthesised zinc carbonate nanoparticles at 120 °C for 4 hours.

4. Conclusion

Zinc carbonate hydroxide nanoparticles have been produced by hydrothermal process. XRD data revealed the formation of $Zn_5(CO_3)_2(OH)_6$ crystal structure from all samples studied. Increasing the hydrothermal processing time from 2 to 4 hours improved the crystallinity of the synthesised particles as indicated by the higher XRD diffraction peaks. SEM images showed that the synthesised particles generally exhibit homogeneous particle size and morphology distributions having spherical shaped morphology and particle sizes in the range of 20-40 nm. There is no significant change observed in size and morphology of the particles synthesised at different hydrothermal processing time. TGA analysis showed the typical single-step decomposition process between approximately 180 °C and 350 °C in which $Zn_5(CO_3)_2(OH)_6$ and $Zn_4CO_3(OH)_6{\cdot}H_2O$ decompose to form ZnO with the release of CO_2 and H_2O. The calculated percentage weight loss was 26.9 % which is comparable to the theoretically calculated value.

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