Synthesis of Hydroxyapatite and ZnO Nanoparticles via Different Routes and its Comparative Analysis

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ABSTRACT

Hydroxyapatite (HAp) was prepared from egg shells by various routes using hexane and acetic acid followed by heat treatment. HAp has a wide application in water treatment by removal of metal ions. XRD of the samples showed use of acetic acid followed by high temperature sintering leads to formation crystalline phases of HAp. Strong evidence of $CaCO_3$ in calcite phase was obtained in other samples. Zinc oxide nanoparticles have also been synthesized by different methods such as sol-gel, co- precipitate and green synthesis. The effect of different synthesis methods were investigated using X-Ray Diffraction (XRD). The structural properties of nanoparticles including particle size were calculated from XRD data. The XRD reveals that the prepared ZnO samples were highly crystalline, having wurtzite crystal structure. The comparative analysis shows variations in particle size with different synthesis methods.

Keywords: Hydroxyapatite, ZnO, sol-gel, co- precipitation, green synthesis, XRD.

INTRODUCTION

Hydroxyapetite (HAp) having formula Ca_{10} $(PO4)_6(OH)_2$ have a wide application in water treatment. HAp based filter are used for removal of heavy metal ions from aqueous solutions[1]. HAp – Chitosan nanocomposites synthesized by sol-gel method have been used for the remocal of Cd^{+2} ions in water treatment[2]. HAp has been found in fish bone. Porous structure and crystalline phases of HAp were obtained when heated at 1000 °C. It showed potential in removal of Cr ions from natural river[3]. 3D ordered HAp hollow microspheres were synthesized from soluble bio polymer like polyaspartic acid where initial formation followed by transformation of calcium phosphate spheres were reported[4]. Sintering of HAp and Silica composite nanopowders have led to formation of porous ceramic filters. The water permeated through them was of drinking water quality [5]. Ag_3PO_4/HAP composites were synthesized facilely via in-situ precipitation of Ag3PO4 on the pre-existing HAP nanowires which can be used as water treatment material[6]. Egg shells have been used to synthesize Hap. The egg shells are three layered structure: cutile, spongeous layer and lamellar layer. It consists mostly of Calcium carbonate and small amounts of Calcium phosphate magnesium carbonate and some organic matter. Hydroxyapetite (HAp) are prepared from egg shells in phosphate solution at elevated temperature [7].

The surfaces of the raw eggshells were mechanically cleaned in order to remove the internal crust lining in the shell. Afterwards the eggshells were washed using tap water for about 15 times. The washed eggshells were then subjected to constant stirring for about 15 – 30 minutes .The sample was then placed in an oven at 100C for constant heating for about 6hours.The dried sample (15.4077g) is then mixed with 50 ml acetic acid and 100 ml of distilled water with constant stirring of about 3 hours. The sample is then filtered by using Buckner funnel. The residue is then washed with distilled water for 10 times. The sample is then placed in the oven at 100C for 6 hours. For the thermal treatment of the sample it is placed in the muffle furnace at 150 ^{0}C for 5 hours. The synthesis routes are tabulated below

Proto XRD at Centre of Excellence for Green Energy and Efficient Technology (CoE-GEET) CUJ was used for the XRD studies where monochromatic Cu-K_{α} radiation having a wavelength of 1.54Å was used. The XRD plots of the samples prepared by four different routes given in Fig 1 were indexed from published reports[8]. The peaks in sample A, C and D were of Calcium Carbonate ($CaCO_3$) in calcite phase[9]. Evidence of HAP was obtained in sample B. This section is stored in ref [10].

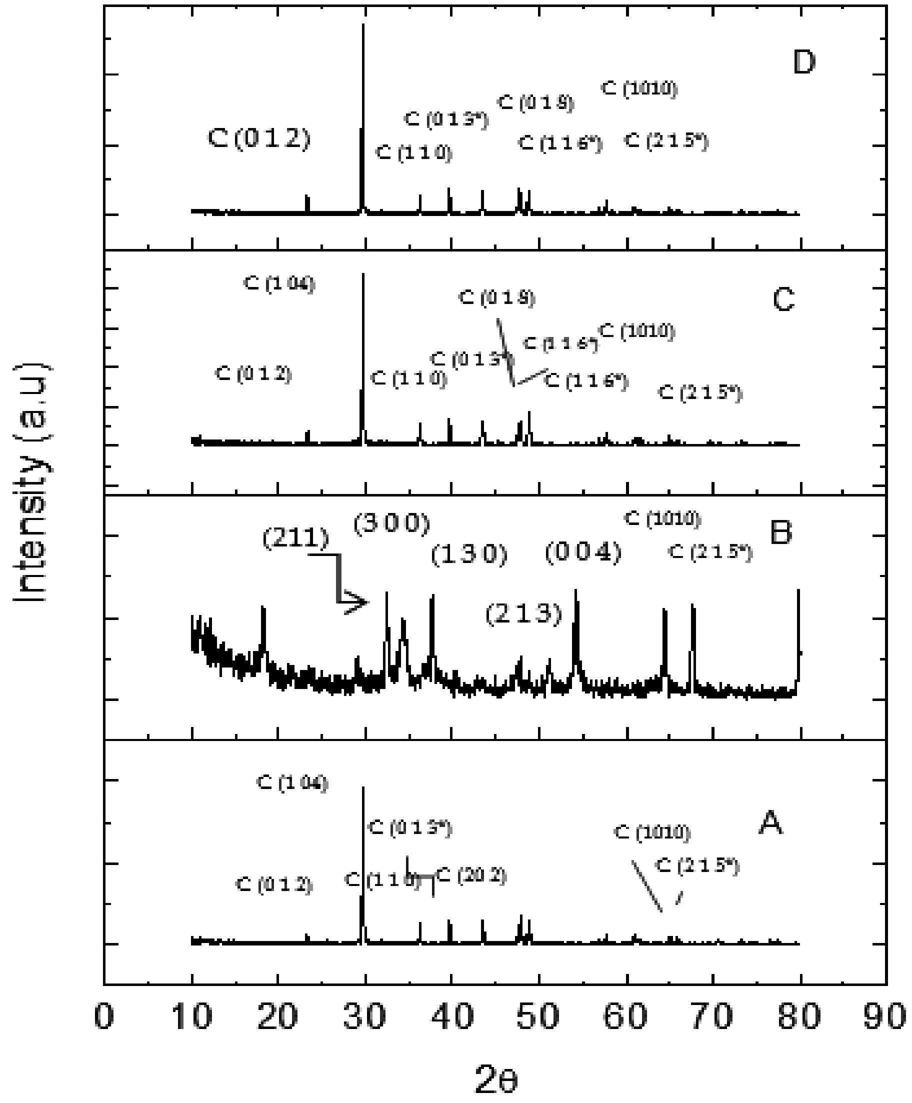

Fig. 1 : XRD of HAp synthesized by various routes

Zinc Oxide (ZnO) has been a promising material showing a lot of application. Various methods and processes have been proposed for its synthesis in nanoparticle form[11]. We have used three different preparation techniques viz Co-precipitation method, Sol-gel and green synthesis and compared the XRD results[12,27].

Preparation of ZnO nanoparticles by Co- precipitation method

The procedure as per ref[15] was followed with slight alterations**.** The solution was prepared with de-ionized distilled water. First of all Zinc nitrate hexahydrate ($Zn(NO_3)_2 . 6H_2O$) of 0.1M (2.97gm) and 0.8M (3.2gm) of Sodium hydroxide (NaOH) were separately dissolved in each 100ml of distilled in 100ml of beaker. And treated by magnetic stirrer. NaOH solution was added dropwise to that solution which produced a white precipitate. The solution with white precipitate was stirred at room temperature for 48 hrs. The solution became dried inside beaker and finally ZnO nanoparticle powder were obtained (Fig 2).

Preparation of ZnO nanoparticles by Sol- Gel method

The zinc oxide nanoparticles were readily synthesized through sol-gel method using zinc acetate as a precursor. The procedure as per ref[19] was followed with alterations in the amount of materials used. In a typical procedure, an aqueous solution made of 1.26g of zinc acetate dehydrate was heated followed by slow addition of absolute alcohol and 600 µL of H_2O_2 (Fig 3) .This solution was dried to obtain white nano zinc oxide[19].

The crystalline structure, morphology of synthesized ZnO nanoparticles were observed using powder X-ray diffraction (XRD).

Fig. 2: Prepared ZnO at Lab by co-precipitation method

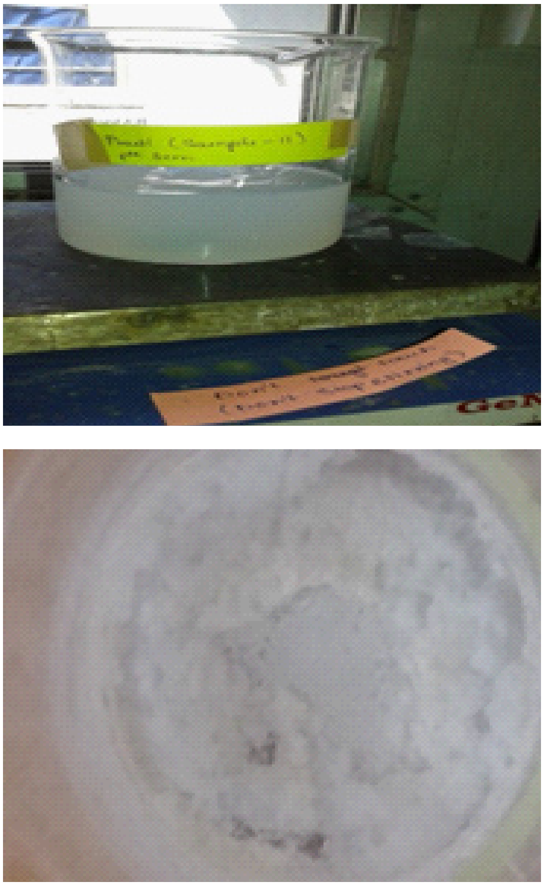

Fig. 3: (a)ZnO solution during preparation, (b) ZnO dried at 80 °C

a

b

Fig. 4: (a) Tulsi Extract T1, (b) Hibiscus Extract (H1, H2)

Table 1: XRD peaks for sample H_1 and H_2

Sample	2θ							
H1	31.88°,	34.46°,	36.41°	47.61°,	56.76°,	62.89	-	68.05	69.21
H2	31.98	34.61	36.48	47.81	56.81	63.06	66.58	68.14	69.33

Table 2: Deconvolution parameters for fig 6

S.No	Area	Centre	Width	Height
1	318.43159867739	31.733467073383	1.0014072109198	253.71462626387
2	604.69553163233	36.765844435967	1.1383215435482	423.84968589106

Preparation of ZnO nanoparticles by Green synthesis method

Sample Hibiscus (H_1)

10ml of Hawaiian hibiscus leaves extract was taken and boiled to 60-80 degree Celsius with a stirrer-heater. About 1.2 g of Zinc Nitrate was added slowly to the resolution as the temperatures reached 60 °C. The procedure followed was as per ref[13].

Sample Hibiscus (H_2)

10 ml of *Hawaiian Hibiscus* leaves extract was again taken and the same procedure was repeated[13]. But this time dilute 1.2 g of zinc nitrate in 10 ml of distilled water was taken and dissolved using magnetic stirrer.

This mixture was then boiled till a deep yellow colored glue was formed which was heat treated at 400 °C for 2 hours. A light yellow colored powder was obtained as reported earlier[13] (Fig 4(b)).

Sample Tulsi (T_1)

The procedure followed was as per ref [14].The leaves of Ocimum Tenuiflorum (Tulsi) were washed and dried in sunlight. And their solution in distilled water was boiled the colour turns in reddish (Fig 4 (a)). The solution was then cooled at room temperature. About 1.2 g Zinc nitrate was further used to form Zinc oxide nanoparticles obtained as light yellow coloured powder as per procedures reported in ref[14].

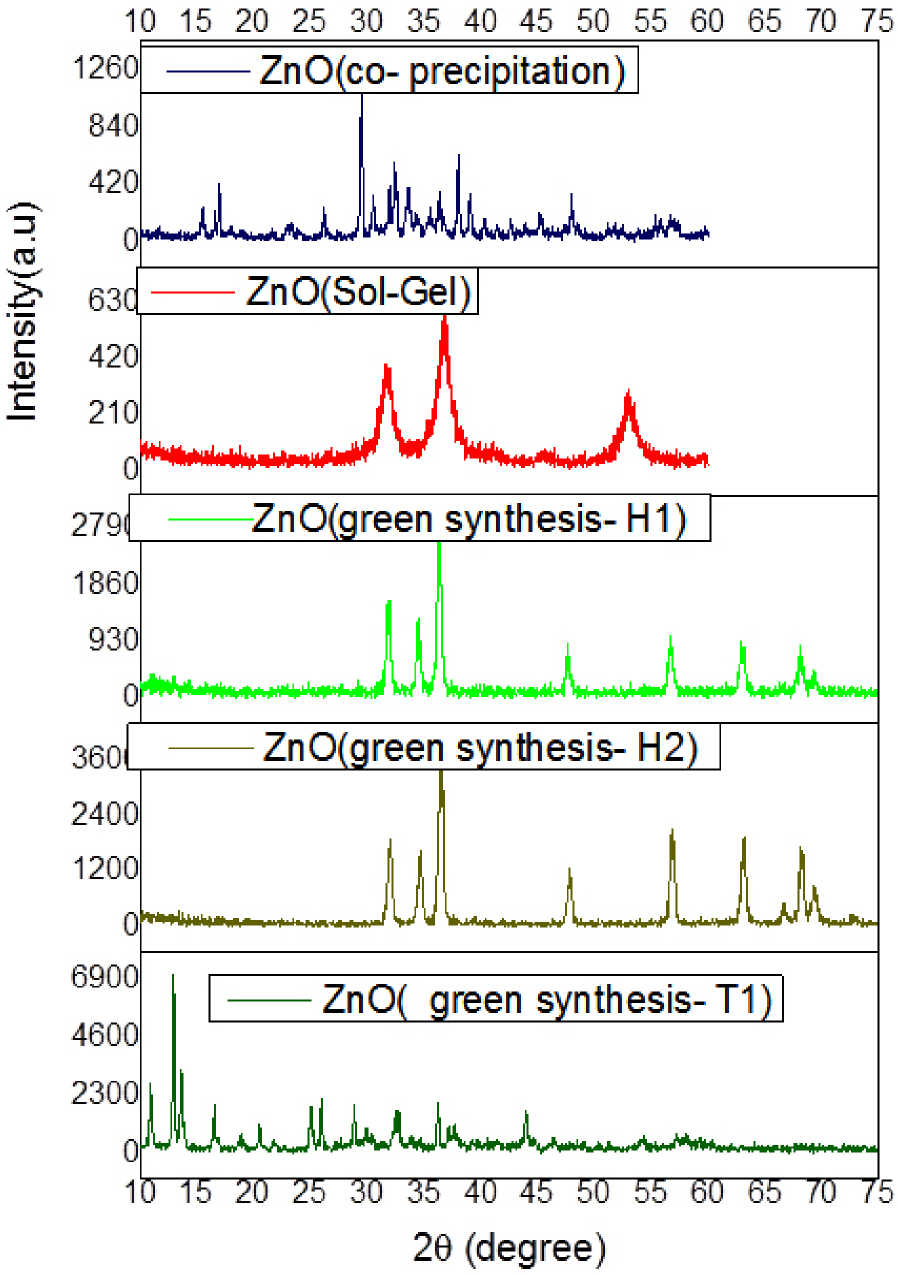

Fig. 5: XRD (multi- curve) of ZnO prepared by different synthesis methods

XRD analysis of ZnO via Co- Precipitation route

Proto XRD at Centre of Excellence for Green Energy and Efficient Technology (CoE-GEET) CUJ (Fig 1) with monochromatic Cu-K_{α} radiation having a wavelength of 1.54Å was used for the XRD studies. Fig 5a) shows the XRD pattern of ZnO synthesized by co-precipitation method where intense and sharp peaks determined its purity and crystalline nature

XRD of ZnO via Green- Synthesis method

For sample H1 & H2, the XRD peaks appeared for 2θ value for H_1 and H_2 as shown in

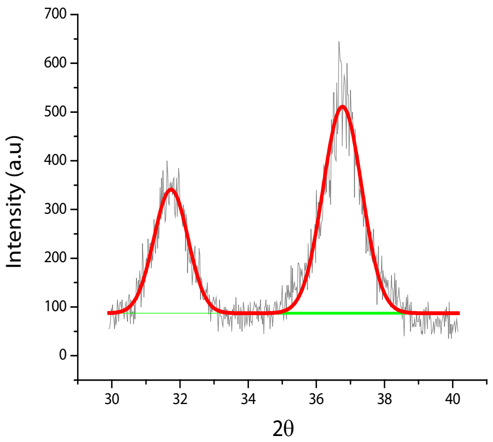

Fig. 6: Deconvolution of XRD of ZnO nanoparticles prepared by sol-gel method

Fig 5 (c, d) are given in Table 2.For sample T1, the diffraction peaks were again intense and sharp in nature indicating formation of multiple phases.

XRD of ZnO via Sol-Gel route

Fig 5 (b) shows a typical XRD pattern of ZnO nanoparticles prepared by Sol-gel route. A deconvoluted peak of the XRD of ZnO-NPs prepared as per sol gel is given in Fig 6 with parameters given in Table 2. Bragg reflections with 2θ values of 31.73°and 36.76° are observed corresponding to (100) plane for peak at 31.73°, (101) plane for intense peak at 36.76° were observed.. Average crystallite size of zinc oxide nanoparticles was determined as 79.25 nm from width of the dominate peaks (100) and (101) reflections according to Debye Scherrer equation. $\boldsymbol{L = 0.9\,\lambda/\beta\ Cos\,\theta}$, where ë is the wavelength of X rays used (1.54060 Å), β is the full width at half maximum (FWHM) = 0.19184 and è is the angle of diffraction. The broadening of the peaks in the XRD pattern can be attributed to the small particle size of the synthesized ZnO.

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