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STARCH ASSISTED SONOCHEMICAL SYNTHESIS OF FLOWER-LIKE ZnO NANOSTRUCTURE

PRIYA MISHRA[*a], RAGHVENDRA S YADAV[a], AVINASH C PANDEY [a, b]
[a]*Nanophosphor Application Centre, University of Allahabad, Allahabad-211002, India*
[b]*Physics Department, University of Allahabad-211002, India*

Flower – like ZnO nanostructures have been synthesized by starch assisted sonochemical method. X-ray diffraction (XRD) pattern indicated that the synthesized flower like ZnO nanostructures were hexagonal. It is found that starch influences the morphology of ZnO structure. On the basis of structural information provided by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM), a growth mechanism is proposed for formation of flower-like ZnO nanostructures.

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1. Introduction

One of the key issues today in nanoscience and nanotechnology is synthesis of nanostructures which are enviornmently benign and have got their shape and size well controlled. ZnO, a II-VI semiconductor material has immense potential applications with band gap of 3.37 eV and large exciton binding energy of 60 meV[1]. ZnO also happens to belong to the richest family of structures among all materials. Various nanostructures of ZnO have been reported like nanotubes [2], nanowires [3], nanodisks[4], nanosprings [5], nanohelix [6], nanoplates and nanosheets[7]. In this work we have used sonochemical method to synthesize flower like ZnO nanostructure with the assistance of starch. Sonochemical method has been known to form novel materials. The chemical effect of ultrasonic irradiation arises from acoustic cavitation which involves the formation, growth and implosive collapse of bubbles in a liquid medium, this process is repeated again and again which result in an instantaneously high temperature and pressure. Starch is one of the most important natural organic compounds abundant in nature. It is a biocompatible polymer and is known to form a wide range of inclusion complexes with several molecules [8]. It is made of repeating units of amylose and amylopectin with alpha 1, 4 linkage between D - glucose units and its molecular formula is $(C_6 H_{10} O_5)_n$. Starch is normally not soluble in aqueous solution of water, however, in presence of both water and heat it becomes gelatinized. Gelation temperature of food starches is between 60 ˚C to 85 ˚C. Gelation of starch plays an important role in controlling morphology of nanoparticles.

2. Experimental

In our experiment, we have used sonochemical method to synthesize ZnO nanostructures using a

sonochemical bath and have tried to investigate the role played by starch in influencing the morphology of nanoparticles. The experiment is simple and the procedure to prepare is as follows: 0.5 g starch was dissolved in 10 ml of double distilled water. 10 ml, 0.1 M aqueous solution of zinc acetate and 10 ml 1M aqueous solution of sodium hydroxide were added to 25 ml alcohol followed by starch solution. The solution containing beaker was then kept in sonication bath (33 kHZ, 350 W) at room temperature. The white precipitate formed was collected by centrifugation and then thoroughly washed with water followed by alcohol to remove traces of starch and other impurities and then kept in vacuum oven for drying. In another set of experiment all the conditions were kept same however, starch was not added to see the effect of starch on morphology. The crystal structure of ZnO nanoparticles were characterized by X-ray diffraction (XRD, Rigaku D / MAX- 2200 H/PC, Cu K_{α} radiation). Scanning Electron Microscopy (SEM) images were taken on LEO Electron Microscopy Ltd, England and E-SEM images were taken on Quanta 200FEG (FEI company).

3. Results and discussion

Figure 1 shows the XRD pattern of ZnO nanoparticles synthesized in presence of ultrasonic irradiation with starch. It can be seen from the XRD pattern that the diffraction peaks are higher and narrower implying that the ZnO crystallizes well and all of the diffraction peaks can be indexed as ZnO with hexagonal phase (JCPDF Card File No. 36145). No characteristic peaks of impurities such as Zn, starch or zinc hydroxide are observed. This confirms that the obtained product contains pure ZnO nanoparticles.

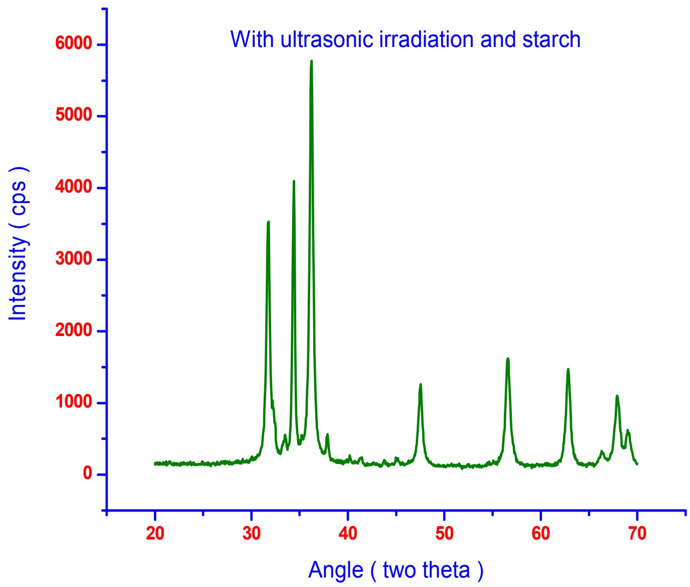

Fig. 1. XRD pattern of flower-like ZnO nanostructure synthesized by starch assisted sonochemical method.

Fig. 2 shows ZnO spherical nanoparticles synthesized in absence of starch using ultrasonic waves. From figure 2, it is clear that there is little agglomeration of particles and have spherical shape. Figure 3 (a) shows ZnO flower-like nanostructures synthesized in presence of starch using ultrasonic waves. Figure 3(b) shows ZnO flower –like nanostructures under high magnification while figure 3(c) shows individual ZnO flower-like nanostructure at high magnification. From Figure 3 it is clear that there are many flat nanorods with pointed ends, are seen to arise from centre, it gives the appearance of a flower, their diameter are several hundred nanometers and length varies from several hundred nanometers to 1µm and the average size of whole flowers is about 1.5μm. Cavitation which occurs during ultrasonication plays key role in sonochemical synthesis of materials. During ultrasonic cavitation very high temperatures of about 5000K, pressures of about 1800 atm [9-11] are reached followed by release of large amount of energy due to collapse of micro-bubbles. These conditions favour simultaneous gelatinization of starch and formation of ZnO nanoparticles with gelatinized starch granules directing the growth of nanoparticles by binding on its surface. Starch is normally composed of amylose and amylopectin in a ratio of 30:70 or 20:80 with amylopectin found in larger amount. Due to continuous ultrasonication with cavitation phenomenon, starch granules swell, there is loss of both crystallinity and double helical order of amylopectin with the leaching of amylose intothe reaction mixture [12-15]. Amylose has the ability to form coils therefore it can direct the ZnO growth units to take the shape of nanorods while still in the sonochemical bath. However when the reaction mixture was taken out of sonochemical bath cooling takes place and gel can form with free amylose molecules losing energy as temperature decreases and forming hydrogen bonds witheach other as well with amylopectin entrapping ZnO nuclei in the process along with them andforming units of nanorods. These nanorods finally clump together with the help of amylose which normally has glue like property of holding starch gels together and finally giving shape of flower. The distinct advantage of using starch is that it avoids agglomeration of nanostructures. Furthermore, the prepared nanostructures are pure and water soluble and there are lots of hydroxyl groups attached to nanostructures surface for further functionalization.

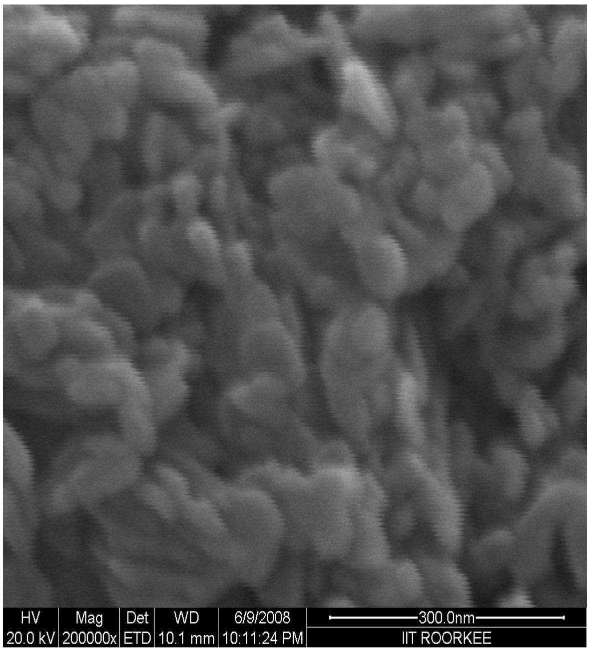

Fig. 2. SEM image of ZnO nanoparticles synthesized by sonochemical method in absence of starch.

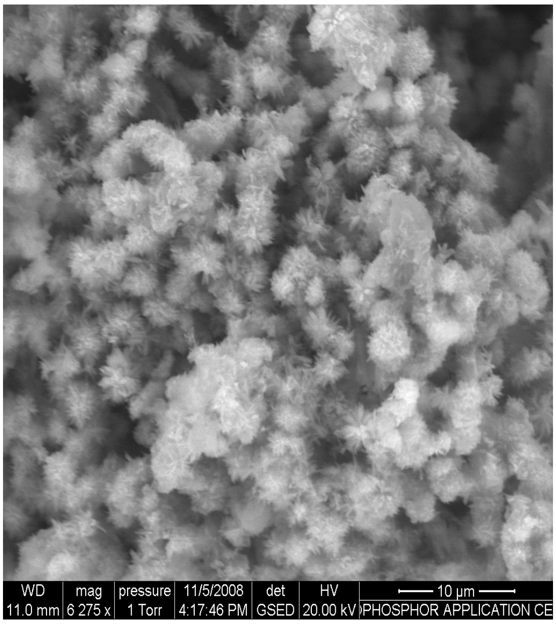

Fig. 3 (a)

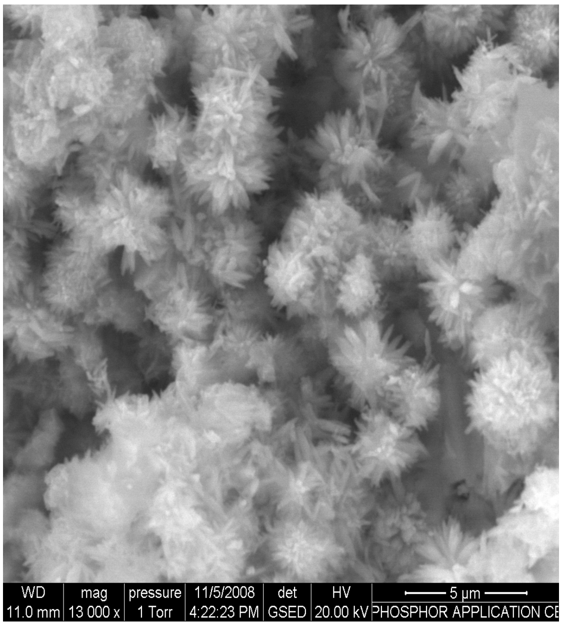

Fig. 3 (b)

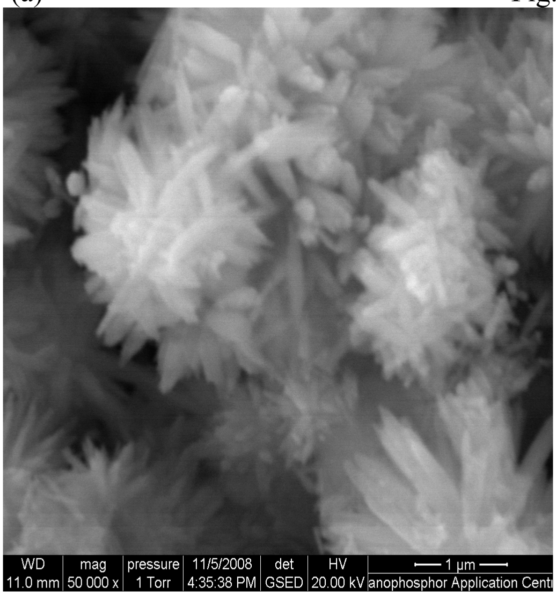

Fig. 3 (c)

Fig. 3 E-SEM image of flower-like ZnO nanostructure synthesised by starch assisted sonochemical method: (a) at low magnification, (b) and (c) at high magnification.

The experimental results show that in formation of ZnO flower -like nanostructure the role of starch should be taken into consideration. In the absence of starch, there is agglomeration of ZnO spherical nanoparticles (fig.2) and in presence of starch flower like morphology is obtained using sonochemical method. The mechanism of formation of ZnO nanoparticles takes into consideration the ionic species formed from water molecules by absorption of ultrasound energy. The reaction steps taking place inside sonochemical bath can be summarised as follows:

$$H_2O \leftrightarrow H^+ + OH^- \qquad (1)$$

$$NaOH \leftrightarrow Na^+ + OH^- \qquad (2)$$

$$Zn(CH_3COO)_2 \rightleftharpoons Zn^{2+} + 2\,CH_3COO^- \tag{3}$$

$$Zn^{2+} + 4\,OH^- \rightleftharpoons [Zn(OH)_4]^{2-} \tag{4}$$

$$2[Zn(OH)_4]^{2-} \rightleftharpoons 2\,ZnO + 4\,H_2O + O_2 \tag{5}$$

Equations (1),(2) and (3) show formation of primary ions which have been formed by dissociation of water, sodium hydroxide and zinc acetate. Equation(4) shows formation of [$Zn(OH)_4]^{2-}$ which further decomposes to give ZnO nanoparticles. In the meantime starch granules (present starch in solution) undergo following process:

$$\text{Starch granules} \Longrightarrow \text{hydration of starch} + \text{leaching of amylose} \tag{6}$$

$$\text{Amylose (glue)} + \text{ZnO nuclei} \Longrightarrow \text{ZnO nanorods} \tag{7}$$

$$\text{Amylose (glue)} + \text{ZnO nanorods} \Longrightarrow \text{Clumping of nanorods into flower} \tag{8}$$

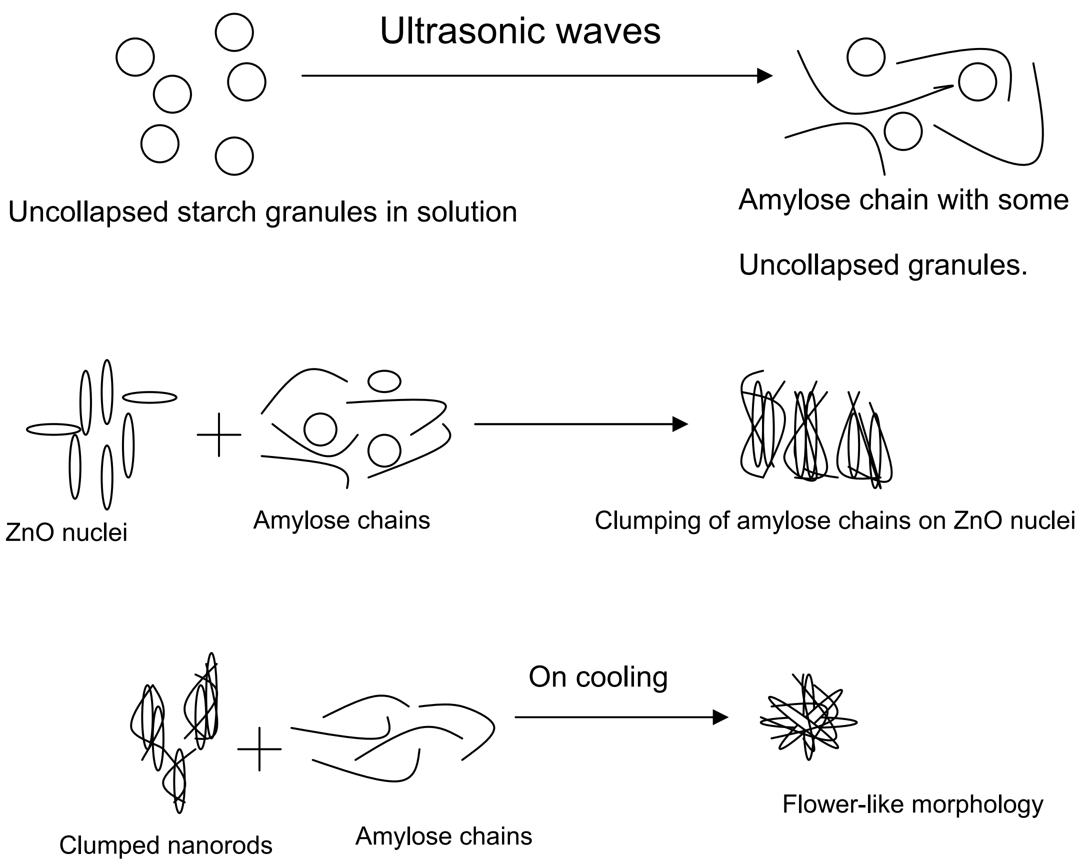

Fig. 4. Diagramatic representation of formation of flower like morphology of ZnO nanocrystals.

Equation (6), (7) and (8) shows that in presence of water and ultrasonic irradiation starch undergoes Gelatinization process during which there is hydration of starch granules, leaching out of amylose and some granules get collapsed. Amylose which comes out has a gluing property it binds on to ZnO nuclei giving it shape of a nanorod as amylose itself has tendency to form coil. When reaction mixture gets cooled these amylose units along with amylopectin and collapsed starch granules form hydrogen bonds among them gluing nanorods together into a spherical structure with nanorods projecting out, giving the appearance of flower as shown in Fig. 4 .

4.Conclusion

We have shown a simple way of synthesizing flower like ZnO nanostructure. The morphology has been well controlled with aid of starch as well as sonochemical method. The nanostructures have been synthesized without the use of toxic material or in other words green chemistry has been used at its best.

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