Solar-assisted synthesis of ZnO nanoparticles using lime juice: a green approach

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Abstract
Zinc oxide (ZnO) nanoparticles are those nanoparticles which have been synthesized in various morphologies and shapes. Their size and shape dependent properties and their applications in vivid sectors of science and technology make them interesting to synthesize. Present work reports a green method for ZnO nanoparticle synthesis using lime juice and sunlight. ZnO nanoparticles were also synthesized by conventionally used methods like heating, stirring or no heating and/or stirring. The nanoparticles were characterized using different techniques like UV–vis spectroscopy, scanning electron microscopy (SEM), x-ray diffraction (XRD) and dynamic light scattering (DLS). Thermo gravimetric analysis (TGA) was also carried out for the intermediate product to select the calcination temperature. Stoichiometric study reveals that the intermediate product formed is zinc citrate dihydrate. The synthesized calcined nanoparticles have good crystallinity, uniform shape, and high purity and were in the size range of 20–30 nm. These nanoparticles formed agglomerates of various shapes in the size range of 200–750 nm. This process is ecofriendly and is amiable for easy scale up.

Keywords: ZnO nanoparticles, lime juice, sunlight, green method, scale up

Classification numbers: 2.03, 4.02

1. Introduction

ZnO nanoparticles are the multifunctional nanoparticles which have applications in various sectors. ZnO nanoparticles can be used for sensors, for catalysis, as solar selective materials, for hydrogen storage, for photo thermal heating materials in tumor treatment, as electronic and electro-optical devices, in biomedicine, in cosmetics, as biomolecule-functionalized NPs, as UV absorber for textiles etc. Nanosized ZnO can absorb both UV-A and UV-B and can also be used for anti-fungal functions [1]. ZnO is also known to be observed in various morphologies viz. flowerlike, rods, spherical, tetrapods, nanowires [2, 3]. The size and shape dependent applications of ZnO nanoparticles make them interesting for researchers.

The methods used for the synthesis of nanoparticles can broadly be categorized as physical, chemical and biological methods. Physical methods include physical vapor condensation [4] and arc discharge methods [5]. Chemical methods include chemical reduction techniques assisted by thermal energies [6, 7], microwave [8, 9], ultrasound [10], electrochemical method [11], pyrolysis [12, 13] and photochemical method [14]. Biological methods include synthesis using biological agents and microorganisms like bacteria, fungi, or plant extracts [15, 16]. These conventional methods possess certain limitations. Chemical methods are expensive, since they require excess reducing agent for size control. The oxidation products forming during the reaction may pollute the final product and there can be toxic chemical products which make the synthesized nanoparticles incompatible for certain
biological application. Biological methods are known to be really slow. In addition to that, selection of microorganism/plant for ZnO nanoparticle synthesis is a really a tough task. For physical methods, large amount of energy requirement is an issue. Nowadays, researchers are looking for the technologies which are greener and sustainable in nature. Photochemical methods are found to be advantageous over conventional techniques in many ways. These methods offer good size control without the use of excess reducing agents, no specific instrument is required and absorption of the radiation occurs naturally due to the presence of light absorbing species in the reaction mixture [17].

Researchers have put efforts in the synthesis of various nanoparticles using different light sources (halogen bulb, LED, mercury lamp, xenon lamp, fluorescent lamp, astralis 5 gun lamp etc) and natural sunlight. Solar energy can be used as a green, clean and inexpensive irradiation source which is present in abundance. The first study on the synthesis of nanoparticles using sunlight was reported by Sterling and Gallant [18] who synthesized Ag nanoparticles using potato starch, a green reagent. Later, different researchers synthesized Ag nanoparticles under solar irradiation using various green reagents like extract of garlic [19], Withania somnifera leaf [26] (the yield was obtained ~80%) [19]. Green reagents have not been found to be used to synthesize nanoparticles using solar irradiation other than Ag nanoparticles. Chemical reagents were also used to synthesize different nanoparticles like Ag [27–30], Au [23, 25, 29, 31–37], Pd [38–41] (the yield was obtained ~70% [41]), MgO [42], Ag/Au nanocomposites [43], Ag/PVA nanocomposites [44], Ag/Au core–shell type [46], hydrogels with silver nanoclusters [47] using natural solar irradiation.

ZnO nanoparticles have been synthesized using various conventional methods like hydrothermal [47], direct precipitation [48], microwave irradiation (yield ~70%) [49], ultrasonic irradiation [50], chemical method [51]. Photochemically, Sun et al synthesized ZnO and ZnO2 by sol-gel technique by nat. et al irradiation [50], chemical method [51]. Photochemically, Sun et al synthesized ZnO and ZnO2 by sol-gel technique by nat. et al irradiation [50], chemical method [51]. Photochemically, Sun et al synthesized ZnO and ZnO2 by sol-gel technique by nat. et al irradiation [50], chemical method [51]. Photochemically, Sun et al synthesized ZnO and ZnO2 by sol-gel technique by nat. et al irradiation [50], chemical method [51]. Photochemically, Sun et al synthesized ZnO and ZnO2 by sol-gel technique by nat. et al irradiation [50], chemical method [51]. Photochemically, Sun et al synthesized ZnO and ZnO2 by sol-gel technique by nat. et al irradiation [50], chemical method [51].

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Green methods are always sustainably attractive. The functional groups present in the biological extracts play an important role in chemical conversions. Various biological extracts have been used for the synthesis of ZnO nanoparticles viz. orange juice [54], aloe vera [55], madder latex [56], coriander [57], neem [57], Indian copperleaf [58], palm olein [59], rice flour [60], key lime [61], crown lower [62], olive leaf [63], ginger root [64], potato starch [65]. All these reports convey the synthesis of nanoparticles without the details, which can be used for scale-up. A few of them have reported the yield of nanoparticles synthesized, however, no reports have discussed the yield and the cost analysis together.

In the present work we have combined the photochemical and biological methods. ZnO nanoparticles have been synthesized using natural and simulated solar irradiation with lime juice as a reducing and capping agent. The process makes the method completely green, economical and ecofriendly. Though ZnO has wide range of applications, not much work has been done on the synthesis of ZnO nanoparticles using solar energy. Also, the size and shape dependence of wavelength of irradiation light source and mode of energy supplied for ZnO synthesis have not been studied. These aspects have been discussed in this work. This proves the novelty of the work.

2. Experimental

2.1. Materials

Zinc acetate dihydrate and 1,4-butanediol were purchased from S D Fine-Chem Limited, citric acid was purchased from Thomas Baker (Chemical) Pvt. Ltd. Bottled lime juice (Fresh & Pure Lemon juice concentrate, 99.9% pure) procured from ELMAC Agro Mfg. Pvt. Ltd, India was used for all the reactions to ensure the same quality and concentration of juice throughout the experiments. All the reagents used were of laboratory grade and were used without further purification. For some trial reactions, lemon juice was prepared using key limes obtained from the local supermarket.

2.2. Methods

Lime juice contains various organic acids like citric acid, maleic acid and ascorbic acid; the main constituent being citric acid. Its reaction with the precursor zinc citrate dihydrate follows the following reaction scheme

\[
3\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + 2\text{CH}_2\text{COOH} \rightarrow (\text{C}(\text{OH})(\text{COO}) - \text{CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O} + 3\text{CH}_3\text{COOH}.
\]

(1)

\[
\text{Zn}_2[\text{OOCCH}_3 - \text{C (OH)}(\text{COO}) - \text{CH}_2\text{COO}]_2 \cdot 2\text{H}_2\text{O} \rightarrow 3\text{ZnO} + m\text{CO}_2 + n\text{H}_2\text{O}.
\]

(2)

Citric acid and ascorbic acid have been used as reducing agents as well as protective agents earlier [66, 67]. In the present work various conventional (conventional stirring, direct heating, indirect heating, without addition of energy) and unconventional methods (solar irradiation, irradiation using a simulated sunlight) have also been employed for the synthesis of ZnO nanoparticles. The general procedure followed for all the reactions is as described below and it can be expressed schematically as shown in figure 1.

Five grams of zinc acetate dihydrate was dissolved in 50ml of lime juice using a magnetic stirrer, unless otherwise mentioned. Depending on the method being followed, the reaction mixture was kept for the formation of the product for a known time. The reactant-product mixture was then kept idle for 12h to allow the nuclei to mature and then the suspension was centrifuged at 7840g force for 30min to separate out the two phases. The product formed was washed with distilled water and centrifuged; this was repeated thrice to ensure complete removal of the solvent or unreacted precursor from the product. The pale yellow reaction mixture turns milky white indicating the formation of the nanoparticles. The product
was then dried in the hot air oven at 100 °C for 12 h. The formed product was an intermediate product, which was then calcined at specified temperature to get the final product, i.e. ZnO nanoparticles.

The conventional methods of synthesis reported include (i) conventional stirring method, in which reaction mixture was stirred at 250–300 rpm using a magnetic stirrer for a known time period; (ii) direct heating method in which reaction mixture was stirred and heated to 70–80 °C using a hot plate for a known time period; (iii) indirect heating method in which the mode of heat supply was indirect using an oil bath; and (iv) synthesis without supply of any energy in which the reaction mixture was kept idle and stagnant for a known time period.

The main focus of the work was on the synthesis of ZnO nanoparticles using unconventional synthesis methods. These include the synthesis using irradiation of natural and simulated sunlight. For the synthesis using natural sunlight with and without color transparent papers, Fresnel lens was used to concentrate the sunlight since natural sunlight is diffused in nature than UV light in terms of energy. The location of the Fresnel’s lens was maintained such that the focal point lies at the surface of the reaction mixture kept in a beaker. Magnetic stirrer was used to maintain the homogeneity of the suspension. The sunlight concentration ratio for the lens used, is defined as the ratio of the area of the lens to the area of the focal point, was 3184.71. The experimental set up for this method is shown in figure 2.

The reactions using simulated sunlight were carried out using a standard 50 W halogen bulb procured from Osram (680 lm, beam angle 36° with a dichromatic reflector). Dichromatic reflector allows visible light and prevents invisible IR behind it and thus passed light can be used as a simulated sunlight. The bulb was mounted on an arm. The height of the location of bulb was calculated based on the trigonometry using beam angle of the light and radius of the base of the reaction container to achieve maximum yield and better utilization of the total incident light. Reaction mixture was stirred continuously. Figure 3 shows the schematic of the experimental set up used for this method. All the experiments were carried out at Institute of Chemical Technology, Matunga, Mumbai, India 400019 (19.0240° N, 72.8584° E). Experiments based on solar irradiations were carried out on the terrace of the same laboratory.

2.3. Characterization

UV–vis absorption spectra of ZnO nanoparticles were recorded using a Varian Cary Eclipse Fluorescence spectrophotometer. Hydrodynamic size of the particles and particle size distribution curve were obtained using dynamic light scattering technique (DLS) and recorded using a Malvern Zetasizer Nano ZS. To obtain UV–vis absorption spectra, hydrodynamic size and size distribution, ZnO test samples were prepared by suspending them in DI water and sonicating them to form a uniform suspension by breaking the agglomeration.

Figure 1. A flow diagram of general procedure for synthesis of ZnO nanoparticles.

Figure 2. Experimental set up for synthesis of ZnO nanoparticles in natural sunlight using a Fresnel lens.

Figure 3. Experimental set up for synthesis of ZnO nanoparticles using a 50 W halogen bulb without lens.
A JEOL JSM-6380 scanning electron microscope (SEM) and a Tescan Mira 3 field emission gun scanning electron microscope (FEG-SEM) were used to record the actual size and morphology of the nanoparticles. A PerkinElmer’s Pyris 1 TGA analyzer was used to record the thermo gravimetric curve of the formed intermediate product and to select the temperature for calcination. Powdered samples were used for these techniques. Also, ZnO nanoparticles were analyzed by x-ray diffraction (XRD) technique to obtain the crystallite size, structure and constituent of the material using a Bruker D8 Advance x-ray diffractometer. It produces diffraction pattern utilizing copper radiations (1.54 Å). The size of the crystallite and the broadening in the peak in diffraction pattern can be correlated using Scherrer’s equation

\[ d_{hkl} = \frac{K\lambda}{\beta\cos\theta} \]  

(3)

where \( K \) is a shape factor whose value is almost equal to 1 (mostly 0.90), \( d_{hkl} \) is crystallite size, \( \lambda \) is the wavelength of x-ray used (1.54 Å when the source is copper to generate x-rays), \( \theta \) is the half the angle at observed peak position or Bragg angle. The Scherrer’s formula is limited to the powdered sample when the size is in nanoscale.

3. Results and discussion

3.1. Reaction mechanism

5 g zinc acetate dihydrate and 50 ml lime juice was used to carry out most of the reactions unless stated otherwise. The intermediate product was calcined at 1000 °C to obtain the calcined ZnO. Reaction scheme described in equations (1) and (2) follows a path in which Zinc acetate dihydrate converts to zinc citrate complex, which then converts to zinc oxide on calcination. Zinc citrate, which is an intermediate product, is available in three forms: zinc citrate anhydrous, zinc citrate dihydrate and zinc citrate trihydrate. Based on the stoichiometry of the reaction and the data available from the experiments, the intermediate product forming in the reaction was confirmed.

Weight of the intermediate product (actual weight of the sample before calcination, \( W_i \)) and weight of the calcined product (actual weight of the sample after calcination, \( W_f \)) were compared with expected stoichiometric yields. Based on the weight of the calcined product, the theoretical weight of the intermediate product obtained was calculated back using stoichiometry (i.e. predicted weight of the sample before calcination based on the weight of the calcined product obtained, \( W'_f \)). \( W'_f \) was then compared with \( W_i \) and the data was plotted to find the best fit. The plots are shown in figure 4. The intermediate product was found to be zinc citrate dihydrate with the best fit.

3.2. Synthesis using natural and simulated sunlight

3 g Zinc acetate dihydrate was dissolved in 30 ml lime juice and irradiated with natural sunlight for 4 h without stirring. The intermediate product was calcined at 1000 °C as before. It yielded 60.12% of calcined ZnO. Reactions were then carried out to optimize the time of reaction. Reaction mixture was stirred at 250–300 rpm. Yields were observed to be 5.39%, 87.15%, 92.54% and 85.35% for reaction times 15 min, 1 h, 3 h and 6 h respectively (figure 5(a)). More yields for 1 h and 3 h reaction time compared to 4 h duration for the reaction when stirring was employed suggested that stirring plays an important role to ensure complete conversions of the reactants and to keep the product in suspension. From the data of reaction yields (table 1) and considering the losses during handling and separation, 1 h–3 h time was observed to be sufficient to convert the reactant into product quantitatively. 2 h was chosen as a reaction time for experiments using solar energy. Further reactions were carried out at peak solar intensity hours from 11:00 am to 1:00 pm.

The lime juice quantity required for the reaction was also optimized. 5 g zinc acetate dihydrate was added to either 15 ml or 25 ml or 50 ml lime juice and the reaction mixture was stirred continuously and irradiated using concentrated natural sunlight for 2 h. The intermediate product was calcined at 1000 °C. pH was measured for all the reaction mixtures and it was found to be 4.2, 3.82 and 3.25 with the addition of 15 ml, 25 ml and 50 ml lime juice, respectively. The yields of calcined ZnO obtained were 21.02%, 52.61% and 92.18% for 15 ml, 25 ml and 50 ml of juice used respectively (figure 5(b)). The reaction was also tried by adding 5 g zinc acetate dihydrate in 10 ml lime juice, but it could not dissolve zinc acetate dihydrate completely hence more quantities of lime juice were taken for other experiments. From the data of the observed yields, 50 ml of lime juice was taken as a standard for all further experiments.

3.2.1. Experiments with pure citric acid. Also, reactions were carried out using pure citric acid under solar irradiation for 2 h. Quantity of water used in the experiments was also optimized, first by adding 10 ml, 20 ml and 30 ml of water in 5.25 g (molar ratio of citric acid to zinc acetate dihydrate = 2) citric acid and
5 g zinc acetate dihydrate and yields of 64.69%, 63.79% and 10.78% were obtained respectively (figure 5(c)). Reactants were also tried by dissolving in 5 ml of water but it could not dissolve the reactants completely. It suggested that a minimum of 10 ml of water was required for the reaction and yield decreased as we increased the quantity of water. The possible reason might be the energy was taken to boil up the excess water when more water was used. If more water quantity was used than required, the energy supplied to the reaction mixture might be first used to boil the entire quantity of water, evaporate the excess water and less amount of energy contributed for the actual reaction to occur. Hence, minimum quantity of water was selected as an optimum quantity which is sufficient to dissolve the reactants and form a mixture but should not waste energy in boiling up excess water. Citric acid quantity was optimized by carrying out number of experiments. 3 g zinc acetate dihydrate and optimized quantity of water i.e. 10 ml was used for these experiments varying the quantity of citric acid. Yields of calcined ZnO were 73.67%, 91.64%, 64.69%, 53.91% and 49.48% when molar ratio of citric acid to zinc acetate dihydrate used was 0.5, 1, 2, 3 and 4 respectively. The results are shown in figure 5(d) and 1 mol citric acid was

![Figure 5](image-url)  
Figure 5. Optimization studies (a) time, (b) quantity of lime juice, (c) water quantity and (d) quantity of citric acid.

| Table 1. Results for ZnO synthesized using various methods at optimized parameters (5 g zinc acetate dihydrate + 50 ml lime juice, calcination at 310 °C for 55 h). |
|---|---|---|---|---|---|---|
| Reaction | Method of synthesis followed | Water addition immediately after reaction | Yield of calcined ZnO (%) | Size (nm) | SEM image (figure no.) | PDI for DLS | UV–vis absorbance |
| | | | | SEM | DLS | | |
| A | Solar energy | No | 82.48 | 46.43 | 743.1 | 11 | 0.119 | 370.0 | 225 |
| B | Solar energy | Yes | 88.95 | 44.45 | 476.8 | 13 | 0.219 | 375.0 | 220 |
| C | Solar energy + blue color filter | Yes | 86.25 | 20.27 | 729.1 | 14 | 0.307 | 370.0 | — |
| D | Solar energy + green color filter | Yes | 80.32 | 24.67 | 564.4 | 15 | 0.022 | 375.0 | — |
| E | Solar energy + yellow color filter | Yes | 82.48 | 53.37 | 238.3 | 16 | 0.242 | 360.1 | — |
| F | Solar energy + red color filter | Yes | 81.40 | 23.69 | 359.7 | 17 | 0.067 | 370.0 | — |
| G | 50 W halogen bulb | Yes | 88.41 | 61.55 | 232.3 | 18 | 0.249 | 365.0 | — |
| H | 50 W halogen bulb (without water addition during reaction) | Yes | 91.11 | — | 462.7 | — | 0.221 | 370.0 | 225 |
| I | Direct heating | Yes | 84.10 | 29.58 | 672.4 | 19 | 0.330 | 370.0 | 220 |
| J | Indirect heating | Yes | 81.40 | 28.10 | 358.6 | 20 | 0.201 | 370.0 | — |
| K | Conventional stirring | Yes | 83.02 | 24.15 | 358.6 | 21 | 0.158 | 370.0 | 225 |
| L | No source of energy | Yes | 42.59 | — | 319.8 | — | 0.133 | 370.0 | — |
concluded to be an optimum quantity. For reaction with 3 g zinc acetate dihydrate, 1 mol citric acid and 10 ml water, the calcined product was analyzed with XRD, SEM and UV–vis spectrophotometer.

The XRD results are shown in figure 6. The XRD peaks match with that reported for ZnO and show hexagonal crystalline structure with crystallite size 5.71 nm. Synthesized ZnO shows crystal planes (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) when 2-theta was varied from 10° to 80°. All the peaks in the figure match well with the standard JCPDS pattern for ZnO (JCPDS card 36-1451). Also, the possible phases for the product are indexed at the peak location in figure 6. The peaks are sharp indicating good crystallinity of the product. The broadness at the bottom of the peaks shows that the product is of small size. No other peak other than ZnO was observed indicating that the product was pure ZnO without any impurities or unreacted precursor. SEM images for the calcined product were also obtained (figure 7(a)). The particles were found to be of random shape and were agglomerated. The average size of the agglomerated nanoparticles was 1355 nm. The same product was then dispersed in water, sonicated for 2 min to break the agglomeration and dried in hot air oven and again SEM was obtained (figure 7(b)). It showed less agglomeration but the average size (833 nm) did not reduce significantly. The size of nanoparticles was quite large and it can be attributed to the fact that the citric acid was used for the reactions. Lime juice contains other components like ascorbic acid and malic acid. Ascorbic acid is a good capping agent and since we used pure citric acid, the growth of nanoparticles might be uninhibited resulting in larger particles. UV-spectrophotometer was used to check for the maximum wavelength of absorbance. The product was dispersed in water, sonicated and analyzed. UV-vis spectrum was recorded for 200–800 nm regions. \( \lambda_{\text{max}} \) was observed to be 375 nm which matches well with the values reported in literature for ZnO nanoparticles [55, 56, 63].

3.2.2. Experiments with lime juice. To verify the effect of the presence of other constituents of lime juice on the size of the nanoparticles, the product obtained for 5 g zinc acetate dihydrate and 50 ml lime juice under concentrated solar irradiation for 2 h was analyzed in a similar manner. The intermediate product was calcined at 1000 °C for 2 h to get ZnO nanoparticles. FE-SEM image of the calcined product showed that the particles have some facets on the surface and the average particle size obtained was 627 nm (figure 8). Not much difference in the particle sizes was observed for all three cases viz. (i) reaction with citric acid without sonication of the product (figure 7(a)), (ii) reaction with citric acid with sonication of the product (figure 7(b)) and (iii) reaction with lime juice without sonication of the product (figure 8). Hence, the presence of ascorbic acid and/or malic acid could not be the reason for the observed larger particle sizes. The possible reason might be the temperature selected for the calcination of the intermediate product, zinc citrate dihydrate. It was allowing the particles to melt and sinter during the cooling phase, resulting into the larger particles. A study for selection of the calcination temperature and time was carried out and it is described in section 3.2.3. It was thus concluded that calcination should be carried out at 310 °C.

3.2.3. Selection of the calcination temperature and time. The reaction mechanism follows a scheme in which an intermediate product, zinc citrate dihydrate is formed. On calcination it converts to ZnO nanoparticles. Selection of the calcination temperature is an important step. For the reaction between zinc citrate dihydrate and lime juice, the intermediate product was calcined at 500 °C for 2 h. The calcined product was greyish in color. Hence, for the further calcinations, higher temperature 1000 °C was selected which resulted in clear white ZnO nanoparticles.

5 g zinc acetate dihydrate and 50 ml lime juice were mixed and heated using a hot plate. Thermo-gravimetric analysis was carried out for the intermediate product from 30 °C to 900 °C at the heating rate of 10 °C min\(^{-1}\). Results for TGA are shown in figure 9. The plot of weight (%) versus temperature (marked with continuous line) indicates that multistage decomposition of the sample is occurring, but there are no intermediate reactions. The other plot of derivative weight (%) versus temperature (marked with dashed line) indicates that there are four types of decomposition events of the intermediate sample when the sample was calcined. The color variations for ZnO when it was calcined at different temperatures are as shown below (figure 10). The material is stable till 239 °C at which the first decomposition occurs. It continues till 333.8 °C which is also nearly equal to the melting point of zinc citrate dihydrate. The decomposition temperature of zinc citrate dihydrate is 295 °C and melting point is 334 °C. To get ZnO, the intermediate complex must decompose but to get the particles in nano size range the material should not melt. So, it was concluded that material should be calcined at 295 °C < calcination temperature < 334 °C. 310 °C was chosen as a calcination temperature for next experiments.

A test sample was calcined at 310 °C for 2 h, charring occurred and the sample turned brown to black. Another sample was calcined at 310 °C for 10 h, light brown color was observed. The same sample was calcined subsequently for additional 15 h (total 25 h), 20 h (total 45 h) and 10 h (total 55 h) and the color change was observed. The color shifted from brown → light brown → beige → ivory white → off
white for calcination time of 2 h, 10 h, 25 h, 45 h and 55 h, respectively. Calcination time 55 h was chosen for calcination for further studies. Since the sample was put in a crucible, it acted like a packed bed. Due to less surface area exposed, it took prolonged times. A fluidized bed could have completed the calcination within a few minutes.

### 3.2.4. Optimized synthesis protocol.

With the optimized synthesis parameters, 5 g zinc acetate dihydrate in 50 ml lime juice and 2 h irradiation time (for 3 g zinc acetate dihydrate 30 ml was the optimized quantity), studies with lime juice were continued. A reaction was carried out with 5 g zinc acetate dihydrate and 50 ml lime juice under solar irradiation (table 1). In one experiment, the reaction mixture was kept idle for 12 h after the reaction was completed (reaction A). In another experiment, water was added in excess (~100 ml) after the reaction period of 2 h, mixed thoroughly using magnetic stirrer and then the reaction mixture was kept idle for 12 h (reaction B). The product was centrifuged, washed several times, dried and then calcined at 310 °C. Both the samples were analyzed using FESEM.

Figure 11 shows the FESEM images for ZnO synthesized using solar irradiation without using any color filter and when the water was added immediately after the reaction. The calcined product yield was 88.95%. It can be clearly seen from the image that particles of an average size 44.45 nm were obtained. Figure 11(a) shows some particle agglomerations. On further magnifying the image, it was observed that the
particles which were looking like flakes were actually consist of small agglomerates of size 200–400 nm. The surface of these flakes and the attached globules on the same can be seen in figure 11(b) and it can be clearly seen that the surface has a texture like a sheet of nanoparticles arranged in the form of 2D arrays. When stacked up, these sheets formed different structures which are the larger agglomerates. These agglomerations could be deagglomerated using ultrasound. ZnO nanoparticles were dispersed in DI water, sonicated for 10 min to form a uniform suspension and analyzed on UV spectrophotometer. The maximum wavelength of absorbance was observed at 375 nm, which indicated the formation of ZnO nanoparticles. The presence of small shoulder at 225 nm can be attributed to the fact that there was a formation of acetic acid during the reaction (curve a in figure 12(A)). Some quantity of acetic acid might have remained and on dissolution with water it gives the peak at 225 nm because of its presence in the suspension, or it can be attributed to any other impurity present in the sample. ZnO suspension was also analyzed using zetasizer. Hydrodynamic size (diameter) of particles was observed to be 476.8 nm. The larger value might be because of the presence of agglomerations in the suspension.

Furthermore, for the other study where water was not added immediately (reaction B) after the reaction, the FESEM images are shown in figure 13. It shows the average particle size of 46.43 nm. The smaller agglomerations were of size 100–150 nm. The surface of the agglomerates of this sample is also similar to the previous one and agglomerates show nice facets. The size and morphology of the nanoparticles were comparable to that obtained when the water was added immediately after the reaction indicating that the continuation of the reaction after the reaction time also might not be the reason for getting the larger sizes in the previous case, where 5 g zinc acetate dihydrate and 50 ml lime juice was irradiated under natural sunlight for 2 h and the product was calcined at 1000 °C (figures 8(a) and (b)). UV–vis absorbance spectra of the ZnO suspension in DI water is shown in curve b of figure 12(A). The maximum wavelength of absorbance was observed to be 370 nm which indicates the formation of ZnO nanoparticles. Zetasizer report suggested that the hydrodynamic size of particles was 743.1 nm with polydispersity index (PDI) of 0.221 indicating the good uniformity of the suspension.

3.2.5. Effect of color filters. FESEM images of the product obtained with reactions using blue color (reaction C) filter are shown in figure 14. Average size of 20.27 nm was obtained. Particles are uniform in size and spherical in shape. The particles are observed to be agglomerated into globules of size
100–150 nm and larger agglomerates of size in the range 800–900 nm. A UV–vis absorbance spectrum again shows a peak at 370 nm indicating no change in purity with the use of color filters in figure 12(A) (curve c). Zetasizer analysis shows the hydrodynamic size of the particles around 729.1 nm. Also, FESEM images for ZnO nanoparticles synthesized using solar irradiation and color filters viz. green (reaction D), yellow (reaction E) and red (reaction F) are shown in figures 15-17, respectively. The average sizes of the particles were found to be 24.67 nm, 53.37 nm and 23.69 nm, respectively, for green, yellow and red color filter. The UV–vis absorbance for green, yellow and red color filters are shown in curve d, curve e and curve f of figure 12(A), respectively, and it shows maximum wavelength of absorbance at 370 nm, 360 nm and 370 nm for green, yellow and red color filter, respectively. All these values match with the range of wavelength of maximum absorbance for ZnO. Zetasizer analysis report for ZnO nanoparticles synthesized using solar energy and green, yellow and red color filters shows the hydrodynamic sizes of the particles are 564.4 nm, 238.3 nm and 359.7 nm, respectively. From this, it can be seen that the agglomeration was less when yellow color filter was used for the synthesis. Also, the agglomerated particles morphology appears to change with the type of color filter used. The shape of most of the agglomerates formed is tetrahedral using blue color filter, ellipsoidal and distorted ellipsoidal using green color filter, tetrahedral with smoothened edges with red color filter and trapezoidal with yellow color filter. Agglomerates with nearly spherical shape were formed when no color filter was used.

3.2.6. Results with simulated sunlight. A reaction was carried out using simulated sunlight (50 W halogen bulb located at an optimized height based on the geometry of the experimental set up to use the maximum amount of energy. The reaction set up is shown in figure 3. Two different reactions were carried out. In one reaction, zinc acetate dihydrate was dissolved in 100 ml of aqueous lime juice (50:50 lime juice and water), and reaction mixture was irradiated for 24 h (reaction G). Obtained calcined product (yield = 88.41%) was analyzed using FESEM and the results are shown below in figure 18. Granules of particles of average size 61.55 nm were observed. The image could not be magnified again to obtain the particle size, since the particle size was too small to be measured using the available FESEM. Particles were observed to be uniform in size and visibly spherical in shape. UV–vis absorbance spectrum for the nanoparticles was shown.
in figure 12(B) (curve g). The peak at 365 nm indicates the formation of ZnO nanoparticles. The hydrodynamic size of the particles was 232.3 nm.

Another experiment was carried out using zinc acetate dihydrate and bottled key lime juice. No water was added in the reaction mixture during reaction. The reaction was carried out for 9 h and yielded 1.69 g of calcined product (yield = 91.11%). UV–vis absorbance spectrum for the product obtained was shown in figure 12(B) (reaction H). Maximum wavelength of absorbance being 370 nm indicates that the formed product was ZnO. The hydrodynamic size using zetasizer was observed to be 462.7 nm. It can be observed that, presence of water during reaction does not affect much the yields.
3.3. Synthesis using conventional methods

Synthesis using direct addition of energy was carried out by heating the reaction mixture to 80 °C for 1 h using a hot plate stirrer heater assembly which resulted in ZnO nanoparticles of average size 29.58 nm (reaction I). The FESEM images for the nanoparticles are shown in figure 19. The particles are agglomerated into larger sizes. UV–vis absorption spectrum for the nanoparticle suspension in DI water was shown in figure 12(B) (curve i). The peak at 370 nm indicates that the formed particles are ZnO. Zetasizer analysis showed that the particles have hydrodynamic size of 672.4 nm with a good PDI.
The reaction mixture was heated indirectly using a water bath at a temperature to 75–80 °C and was maintained at that temperature for 1 h (reaction J). FESEM images show that particles are visibly spherical and have an average size of 28.10 nm (figure 20). Particles have formed agglomerates of size ranging from 700 to 900 nm. The particles of small sizes are agglomerated to form the small lumps (globules) which again are agglomerated to form even bigger size lumps. UV–vis absorption spectrum showed maxima at 370 nm (curve j in figure 12(B)). The suspension was observed to have good PDI and particles have hydrodynamic size (diameter) of 358.6 nm.

Reaction was also carried out using only stirring (reaction K). The reaction mixture was kept under stirring at 250–300 rpm for 9 h and then water was added to prevent the growth of the nanoparticles. ZnO particles formed (yield = 83.02%) by this reaction were also similar to those formed using other reactions. The particles were observed to be spherical and uniform in size. Particles of average size 24.15 nm were obtained which agglomerated into small and large agglomerates as shown in FESEM images (figure 21). UV–vis absorbance spectrum shows maximum wavelength of absorption at 370 nm (curve k in figure 12(B)). The hydrodynamic size of particles was observed to be 352.6 nm.

Reaction was carried out without the addition of any energy. Zinc acetate dihydrate was dissolved in bottled key lime juice and kept idle for 12 h. Water was added in the reaction mixture after 12 h to prevent further growth of formed nanoparticles. After calcination, the product yield was found to be 42.59%. The formation of nanoparticles even when there is no supply of energy can be attributed to the fact that the conversion of citric acid to citrate ions and vice versa in aqueous medium is easy with requirement and/or release of reasonable amount of energy (ΔG ~ 47 kJ mol⁻¹) [54]. This energy might be sufficient for ZnO nanoparticle synthesis. The peak at 370 nm in UV–vis absorption spectrum indicates the presence of ZnO nanoparticles (curve 1 in figure 12(B)). The hydrodynamic size of particles was 319.8 nm.

All the results for the methods used for synthesis of ZnO nanoparticles using lime juice at optimized parameters are summarized in table 1.

4. Conclusions

A simple, green, ecofriendly and additive free method has been reported for the synthesis of ZnO nanoparticles using solar energy and lime juice along with the conventional methods. The following overall conclusions can be drawn from the experimental and results reported in the present work:

(a) Lime juice can be a green source which can be used as a reducing as well as capping agent for the synthesis of ZnO nanoparticles. Citric acid present in lime juice was found to form zinc citrate as an intermediate. Citric acid and citrate ions are interconvertible in the aqueous medium and it releases sufficient amount of energy which could progress the reaction even in the absence of any external source of energy. Calcination of this intermediate yields ZnO. Calcination at 500 °C yielded grayish product.

(b) High quality product was obtained using pure citric acid as a reducing and capping agent when calcined at 1000 °C and yielded larger size particles and agglomerates. The agglomerated particles could not be broken even using sonication. The presence of ascorbic acid in the lime juice was thought to be a good controlling agent for particle size.

(c) The intermediate product was found to be zinc citrate dihydrate based on a stoichiometric study. The calcination temperature was checked by carrying out TGA of the sample and 310 °C was fixed as a calcination temperature, as the product start decomposing at 240 °C and it melts at 334 °C. So, to prevent sintering of the nanoparticles the product was calcined at a temperature lower than the melting point. To obtain better quality of ZnO nanoparticles, the calcination time was extended upto 55 h.

(d) The nanoparticles now obtained are in the size range of 20–50 nm. All the reactions yielded ZnO nanoparticles as shown by UV–vis absorption spectra where maximum wavelength of absorption is in the range 355–380 nm. The shape of the nanoparticles was found to be independent of energy source or wavelength of the light used. But the morphology of the agglomerates was observed to be
different for different source of energy used during reactions. Moreover, ZnO nanoparticles synthesized using yellow color filter, were observed to have largest size. But the aggregate size of the same was observed to be the minimum among the particles synthesized using solar energy.

Solar energy is a clean energy and it can be used to synthesize ZnO nanoparticles with high purity, smaller sizes, crystalline in nature and narrow size distribution. Using key lime juice for the synthesis makes the method green and eco-friendly. Moreover, the effect of different wavelengths of sunlight on the shape and morphology of nanoparticle was not observed to be a dominant factor, though the morphology of the agglomerated forms were not the same. Hence, nanoparticle synthesis using unconventional source of energy, specifically solar energy is a promising method.

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