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Biopolymer-Based Green Synthesis of Zinc Oxide (ZnO) Nanoparticles

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Biopolymer-Based Green Synthesis of Zinc Oxide (ZnO) Nanoparticles

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Abstract. The use of biopolymers for the synthesis of various nanomaterials is of huge interest to present day nanobiotechnology. A basic, novel, cost effective and green method has been developed for the synthesis of ZnO-NPs (zinc oxide nanoparticles) utilizing carrageenan as a marine biopolymer. This work suggests the use of green method serving carrageenan as a stabilizing agent during sol-gel process before calcination in high temperatures to generate ZnO-NPs. The produced ZnO–NPs were characterized using various tools such as powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), Fourier Transform Infrared (FTIR) and UV–visible (UV–vis) spectroscopy. The ZnO-NPs synthesized at various temperatures displayed spherical structure, its TEM images and particle size distributions exhibited the size of 49 nm. The X-ray diffraction (XRD) analysis showed the successful synthesis of ZnO-NPs with high purity and crystallinity. The UV-visible spectra showed characteristic absorption peaks of ZnO between 368 and 376 nm and FTIR analysis exhibited Zn-O bands around 402 to 448 cm^{-1}. The biosynthesized ZnO-NPs could offer potential applications in bio-medical field.

Keywords: Green synthesis, ZnO nanoparticles, carrageenan, biopolymer, transmission electron microscopy.

Introduction

Over the last decade, nanotechnology has gained great attention for their ability to manipulate and fabricate devices and materials on the scale of less than 100 nm. [1, 2] . The origin of term nano started from the Greek word "nanos" meaning "dwarf" [3]. Nanotechnology deals with materials having nanoscale in one dimension ranging between 1 to 100 nm [4]. It involves modifying or developing materials within that size, making them stronger, lighter, smaller, faster, and more durable. Nanotechnology has been role player in various areas such as engineering, biology, chemistry, medicine, modelling, and in bio-processing industry. These applications depend on few factors like higher surface area, physical features, and nanoscale size which offer opportunities for control and leads to numerous functionalities [5]. New advances in the field of nanotechnology, especially the ability to produce planned nanoparticles of any shape and size, have brought new developments of biomedical agents. [6, 7]. Nanomaterials with new biomedical properties are also known as "a wonder of medicine" in the world of medicine. [6].

Metal oxide nanoparticles have an important role in various fields of chemistry, physics, and materials science [8]. Metal oxide nanoparticles (NPs) have attracted great research interest due to their outstanding properties like optical, magnetic, catalytic and optical [9]. The metal componentss are able of forming huge variety of oxide compounds. These can receive a wide number of auxiliary geometries with an electronic structure that can show insulator, semiconductor and metallic character.

Among the metal oxide nanoparticles, zinc oxide (ZnO) is fascinating due to its high photosensitivity, physical and chemical stability, non-toxicity as well as wide band gap [6]. In addition, it has tremendous applications in different fields such as dyes, pharmaceuticals, perfumes, biology, petroleum, and agrochemicals, fragrances, colors, petroleum and science due its less toxicity in vivo and vitro. The application of ZnO as antibacterial agent has gained great attention recently in the field of microbiology for the development of biomaterials due to its high biocompatibility, stability, quick electron transfer and longer life than organic based disinfectants. [10]. ZnO nanomaterials are being extremely significant for the use in a vast biological applications counting cancer treatment, drug delivery, antimicrobial agents and bio imaging probes [11]. Studies have proven that ZnO is fatal to cancer cells [12] . ZnO nanoparticles has the ability to produce ROS (reactive oxygen species) while responding to cell membrane lipids showing higher toxicity against cancer cell in vitro [13]. Generally, the bulk ZnO is recognized as safe substance according to the US Food and Drug Administration (FDA), ZnO nanoparticles larger than 100 nm supports its use for drug delivery which is considered relatively biocompatible [14]. Normally, 10-15 mg of Zn is required daily for the physiology and typical growth of the human being [15]. Many studies have shown that cancer cells are very susceptible to ZnO toxicity at a concentration dependent manner and time. Besides that, ZnO nanomaterials show high catalytic efficiency, solid adsorption capacity and are utilized increasingly as often as possible in the fabrication of rubber processing, fungicide, wastewater treatment, sunscreens and ceramics.

There are a wide cluster of reports accessible on the preparation of zinc oxide nanoparticles (ZnO-NPs) utilizing diverse methodological approaches like solvothermal and hydrothermal synthesis [16], precipitation [17], polymerization method[18], laser ablation [19] , microwave irradiation [20], wet chemical method[21], photochemical method[22], sonochemical [23], and sol gel methods[24]. Yet, use of such techniques suffers various downsides like utilization of high pressure and temperature, lengthy reaction time, hazardous reagents, needs of external additives particularly stabilizer, promoter or base throughout the reaction which restricts the purity of ultimate product. Overall, the synthesis of nanoparticles is a complex process, and a huge wide range of factors may influence the properties of the final outcome with preparation of various methods. Moreover, chemical methods might cause the presence of some toxic chemicals adsorbed on the outer surface of ZnO-NPs that may have side effects in medical applications [25]. It is most essential to synthesize ZnO-NPs by a simple, eco-friendly, low cost process that can produce stable nanomaterials in nano-size. Natural polymers of gelatin, starch, and different proteins are all fascinating materials in the manufacture of nanomaterials since they are bio-absorbable and biodegradable [26]. On the other hand, nanomaterials synthesis using other biological entities such as microorganisms, enzymes, and algae can be hazardous and costly [27].

Using natural polymers have a eco-friendly and low cost approach in the synthesis of nanomaterials [26]. Many natural polymers are being used in the synthesis of nanoparticles as a green stabilizer [22]. Carrageenan is an eco-friendly polymer derived from a class of red seaweed. Carrageenan has worthy biological functions due to its high viscosity and superior gelling features [28]. Few biological properties of carrageenan like anti-inflammation, antiviral, antitumor, immunomodulatory, antioxidant, and anticoagulant activities might make huge changes in medical application [29].

ZnO has doubtfully large applications in many areas such as magnetic, optical, food packaging industry, piezoelectric, cosmetics, and gas sensing. Beside these applications, ZnO-NPs are also used in biomedical applications including anticancer [30], antibacterial [31], antioxidant [32], anti-inflammatory [33] and antifungal [34] uses. Recently, ZnO is listed as a safe substance supporting for its use for drug delivery by Food and Drug Administration [35]. The present research area utilizes carrageenan as a stabilizing agent to produce ZnO-NPs via green synthesis method. ZnO-NPs were successfully synthesized by thermal decomposition technique at various temperatures. The aim of this work was to employ an easy method for the green synthesis of ZnO-NPs and investigate their physicochemical properties.

2.1 Material and Reagents

Zinc nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$ (98%) was used as a zinc ion source to biosynthesize ZnO-NPs along with carrageenan (chemically pure). All chemicals were purchased from R&M Chemicals, United Kingdom and utilized without further purification. Throughout the experiment, aqueous solutions were prepared with deionized water and clean glass wares were used.

2.2 Green Synthesis of Zinc Oxide Nanoparticles

ZnO-NPs were green synthesized using sol-gel technique followed by thermal decomposition method. Firstly, 4.5 g of zinc nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 10 ml of deionized water. Simultaneously, carrageenan solution was prepared by adding 0.2 g of carrageenan powder into 40 ml of distilled water under steady stirring until it forms homogenous solution. Carrageenan acts as a stabilizing agent during the sol-gel process to control particle sizes of ZnO-NPs. Next, both carrageenan solution and zinc nitrate solution were mixed and continuously stirred at 75 °C for 8 hours. The final ZnO nanoparticle is product through calcination at the temperature of 500 °C using furnace.

2.3 Characterization methods and instruments

The green synthesized ZnO-NPs will be characterized using ultraviolet-visible (UV 2600, SHIMADZU) spectroscopy (UV-vis) between 300 nm to 550 nm to observe their absorption peaks. ZnO-NPs will be studied through X-ray diffraction (XRD, Philips, X'pert, Cu, Ka) at the small angle range of 2Θ (20°-100°). To study the functional groups present on the biosynthesized ZnO-NPs, Fourier Transform Infrared spectroscopy (FTIR) will be set to run between of 400-4000 cm^{-1} using Series 100 FTIR spectrophotometer (IRT racer-100, SHIMADZU). KBr pellet method will be used to prepare the tablet by mixing potassium bromide and ZnO-NPs sample then ground to become fine powder. Finally, morphological study of the ZnO-NPs structures was done using Transmission Electron Microscopy (TEM) (model JEM-2100 F).

3. Results and Discussion

In this project, a simple method to synthesize nano-sized ZnO using green compound has been well demonstrated by utilizing carrageenan. Carrageenan, a water-soluble polysaccharide originated from red seaweed has been proven to be effective in controlling morphology of nanoparticles [36]. Vinyl sulfonic acid functional groups found in carrageenan structure interacts with the Zn^{2+} ions, preventing them from aggregating during the sol-gel process [36]. After that, nano-sized ZnO are formed through calcination process in high temperature as shown in **Fig. 1.**

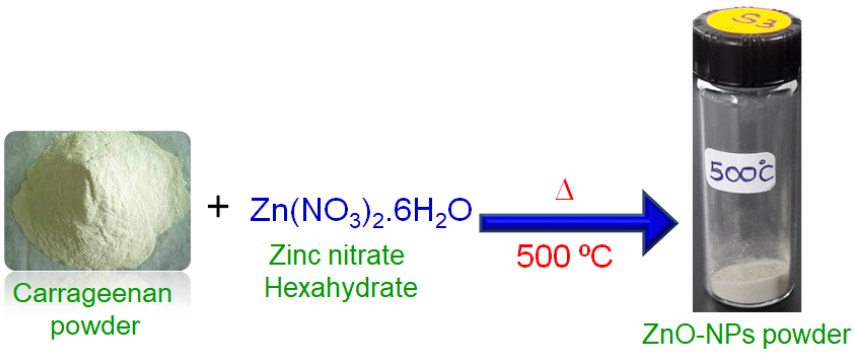

Fig 1. Image of green synthesized ZnO-NPs at 500 ºC temperature.

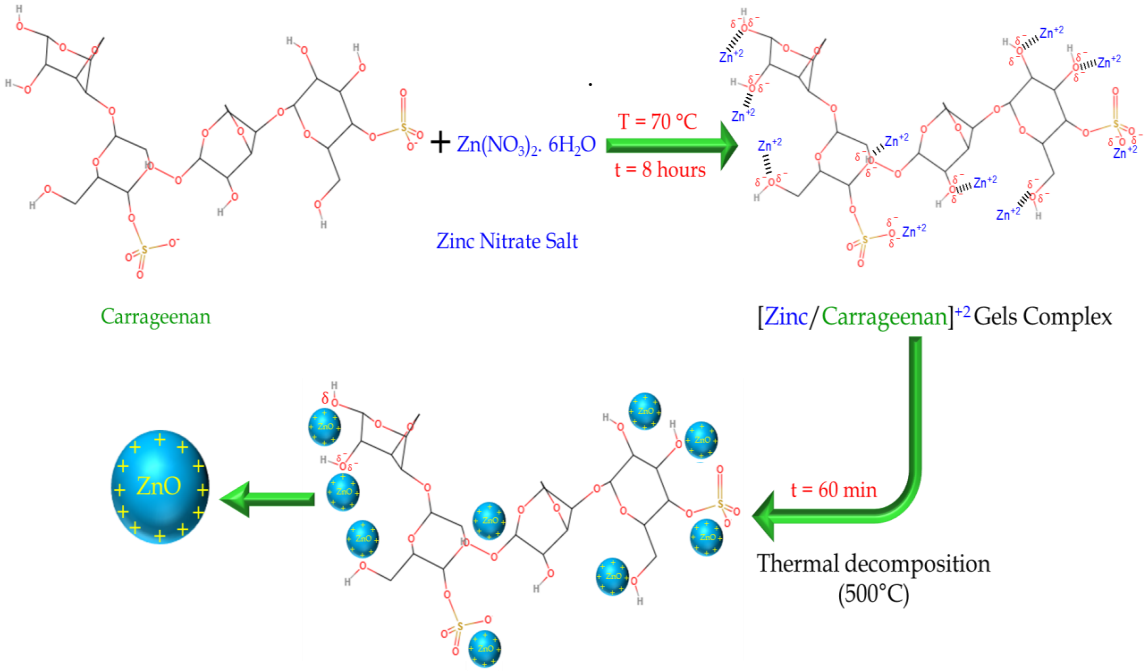

Fig 2. Illustration of ZnO-NPs synthesized mediated by carrageenan as a biopolymer.

3.1 X-ray Diffraction Analysis

The Miller indices peaks obtained from XRD analysis of all biosynthesized ZnO-NPs are shown below in Fig. 3. The obtained results show the sample of ZnO-NPs with the same peaks that is in great agreement with those in the JCPDS card (Joint Committee on Powder Diffraction Standards, Card No. 89-1397). Thus, it is confirmed that the biosynthesized ZnO-NPs are highly pure and free of impurities as it does not contain any characteristics Miller indices peaks other than zinc oxide peaks [5]. The diffractogram peaks at 2θθ values of 32.00º, 34.53º, 36.35º, 47.65º, 56.68º, 63.05º, 66.53,º 68.05º, 69.27º similar to the crystal planes of (100), (002), (101), (102), (110), (103), (200), (112) and (201) respectively. The sample exhibited intense and narrow peaks, which means it has high crystallinity.

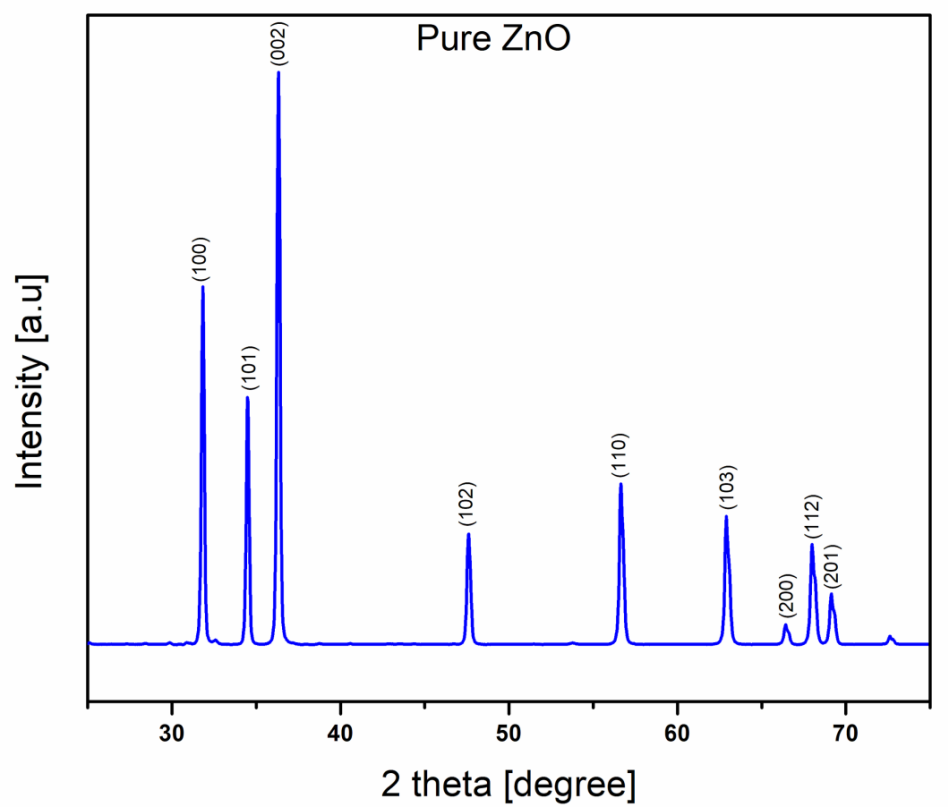

Fig. 3. XRD graph of ZnO-NPs calcined at 500°C.

The crystallite sizes of biosynthesized ZnO-NPs were calculated using Debye Scherer formula shown in **Eq. (1)**. Average crystallite size of all ZnO-NPs was calculated to be 49 nm using the Debye Scherer formula.

$$\text{Crystallite size} = 0.9 \times \lambda / \beta \times \cos\theta \quad (1)$$

Where λ = X-ray wavelength

β = Line broadening at half the maximum intensity (FWHM)

θ = Bragg angle

3.2 UV – visible (UV-vis) Spectroscopy Analysis

The optical absorption spectra for biosynthesized ZnO-NPs were recorded using UV-vis spectroscopy in the range of 300-600 nm as shown in **Fig. 4**. UV-vis spectra display absorption peak at 378 nm for ZnO-NPs calcined at 500°CIn most cases, it comprises an ultra violet emission peak within the range of 370-390 nm, together with a broad visible emission band centered at around 500-560 nm, related with oxygen vacancies [20].

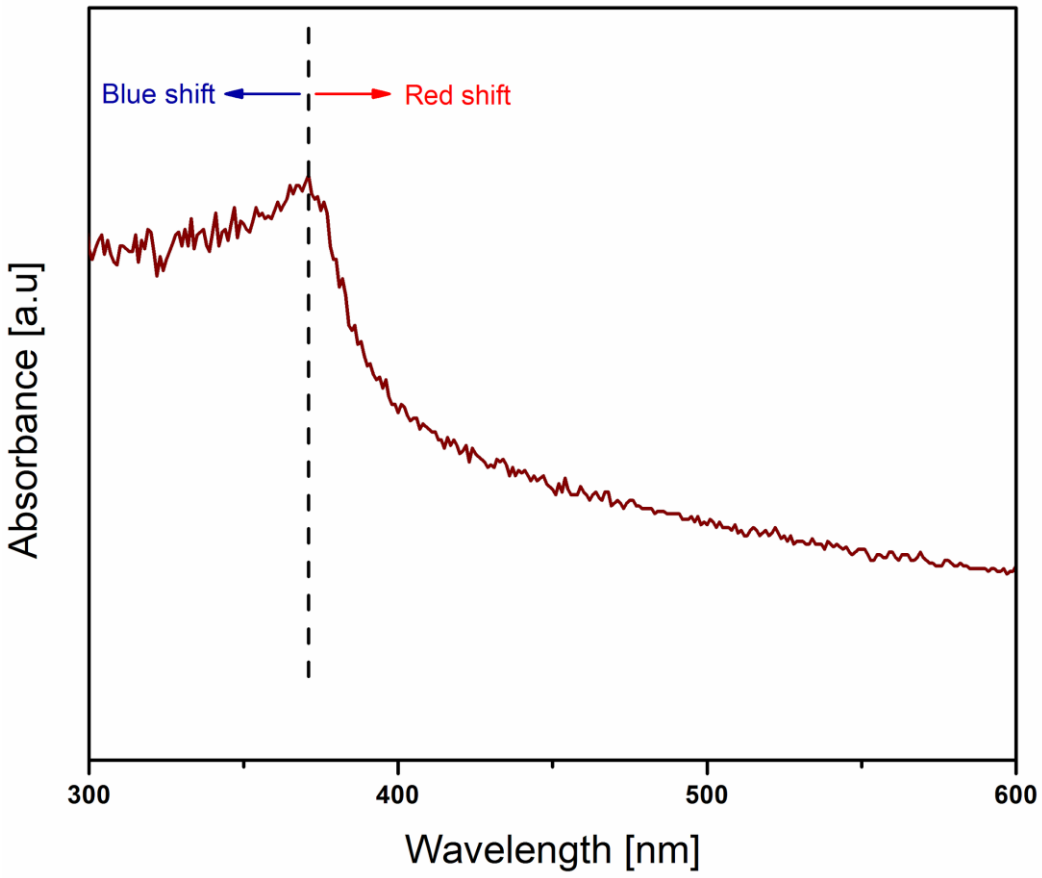

Fig. 4. UV-vis spectrum of ZnO-NPs calcined at 500°C.

3.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectra were run in solid phase using the KBr pellet technique in the range of 400-4000 cm^{-1} to observe any functional groups in all ZnO-NPs samples. The absorption bands are labeled as shown in **Fig. 5** for produced ZnO-NPs. More specifically, the peaks observed at 2370, 3450 cm^{-1} was assigned to N-H stretching. The peak at 1640 cm^{-1} is related to N-H bending for primary and secondary amides. The peak at 1382 cm^{-1} is related to C-F. At 1100 cm^{-1} the peak is related to C-O. Characteristic ZnO absorption band can be seen in the region between 402 and 448 cm^{-1} for this sample. For ZnO-NPs calcined in higher temperature, more intense bands as well as Zn-O bond stretching can be observed.

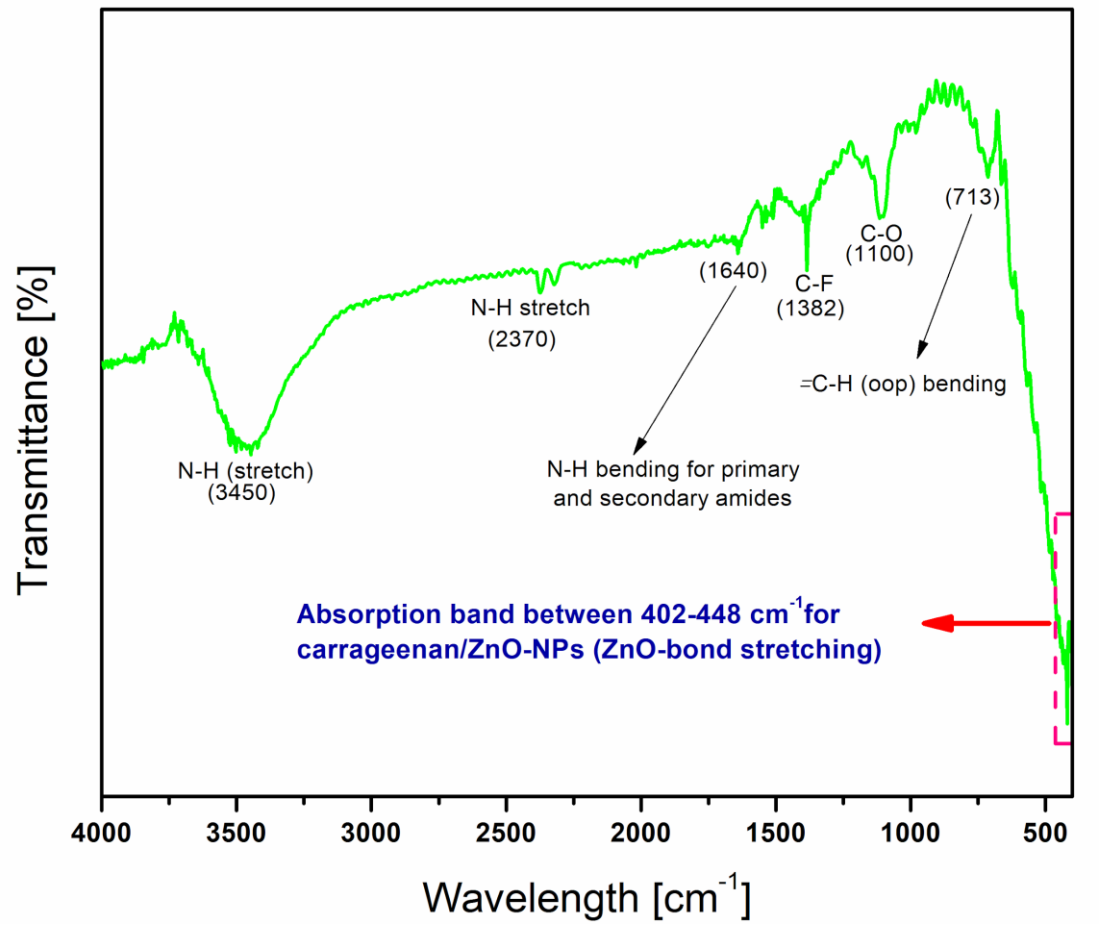

Fig. 5. FTIR spectra graph of ZnO-NPs calcined at 500°C.

3.4 Morphology study of Zinc Oxide Nanoparticles

Further characterization using Transmission Electron Microscopy (TEM) was carried out for ZnO-NPs samples calcined at 500 °C to study their morphology. TEM images and their respective particle size distribution for ZnO are shown in **Fig. 6**. It can also be observed that circular shapes were exhibited. Histogram of particle size distribution was plotted and average size of ZnO-NPs was measured. The mean diameter and standard deviation of ZnO-NPs was about 49±12. The particle size is match with XRD results based on Debye Scherer formula.

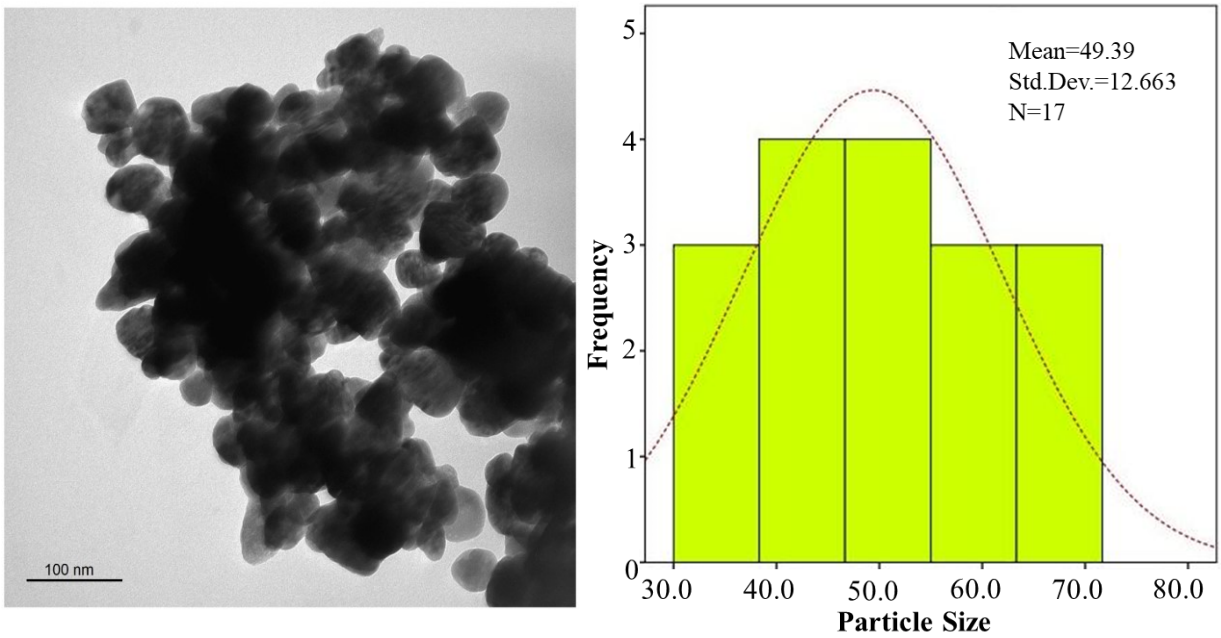

Fig 6. TEM image of ZnO-NPs at 500 °C with respective particle size distribution histogram

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4. Conclusions

This work has presented a simple, green approach to synthesize ZnO-NPs by utilizing carrageenan as a stabilizing agent during the sol-gel process and then calcination in high temperature. The XRD results showed that green synthesized ZnO-NPs displayed spherical structure with high purity. This method is interesting in the synthesis of nanoparticles which is low cost, simple and environmentally friendly. A further study of these nanoparticles in the medical application is expected to be conducted.

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