

## Zinc Oxide Nanoparticles: chemical, physical and Biosynthesis Synthesis and its some Applications

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**Abstract:** This review article described the major synthesis of Zinc oxide nanoparticles with various ways, such as physical synthesis, chemical synthesis and Biosynthesis. Chemical synthesis as Hydrothermal Technique, Vapor Transport, Precipitation Method, Self-Combustion technique, Sol-gel method and microemulsion method. Physical synthesis as high-energy ball milling method, laser ablation method and Physical vapor deposition method. Biosynthesis Includes synthesis through fungi, plants, bacteria Some applications of zinc oxide nanoparticles have been listed.

**Keywords:** Zinc oxide; Biosynthesis; metal oxide; nanoparticles

### 1. Introduction

In the last years nanotechnology research has obtained attention by presenting innovative solutions in the area of materials science, biomedical, optics and electronics<sup>37</sup>. The growth, processing and characterization of nanoparticles is of global attention at present. Nanostructured materials received this attention because of their special performance in photonics, optics and electronics<sup>10</sup>. NPs are basically by modify their atomic and molecular properties of elements and in nanotechnology is a small substance behaves as a complete unite in field of its properties and transport<sup>23</sup>.

Study in the domain of preparation methodology of particles is at most depend on controlling their composition, shape and size. All of these factors are important in determination the specifications of particles that driving to various technology applications.

ZnO NPs were prepared by various and several method such as precipitation method, spray pyrolysis method, microemulsion method, hydrothermal method and sol gel method<sup>20</sup>.

Zinc oxide is an inorganic compound with the molecular formula ZnO. It shows up as a white powder and is almost unsolvable in water. Zinc oxide (ZnO), a II–VI compound semiconductor with a wide and a direct band gap of 3.37 eV at room temperature, is perceived as one of the most encouraging materials for ecological insurance applications related to risky waste remediation, air purification, and water purification<sup>14, 46, 47</sup>. ZnO has different properties, for example, biocompatibility, cost effective syntheses, and so on. ZnO is a standout amongst the most encouraging multifunctional semiconductors.

In nanostructure frame, ZnO uncovers an extensive variety of growth morphologies, such as nanowire, nanoring, nanotube, nanohelix, nanocage, nanobelt, nanosphere, nanodisk, and nanorod<sup>8, 31, 43</sup>. ZnO semiconductor has a special properties, for example, great transparency, high electron versatility, wide band gap, and stro in transparent electrodes in liquid crystal display and in energy-saving or heat-protecting windows and other electronic applications. These days the one of a kind properties of nanomaterials have roused the scientists to create numerous less difficult and cheap strategies to deliver nanostructures of technologically important materials. Several metal oxide nanoparticles are produced with conceivable future applications. Among them zinc oxide is thought to be one of the best exploited at nanodimensions. The wide band gap and large excitonic binding energy have made zinc oxide important both for logical and mechanical applications<sup>42</sup>. Zinc oxide is a multi practical material since it has unparalleled properties whether chemical or physical, for example, high photostability, high conduction stability, wide range of radiation absorption and high electrochemical coupling coefficient<sup>12</sup>.

Due to the importance of zinc oxide nanoparticles in particular in many areas of life and their widespread use and unique features, and the need for many research to prepare it in the simplest and most effective way has been prepared this study which provides a comprehensive review of the current research activities that focus on the ZnO NPs. The present review aims to describe and discuss the different methods used for synthesis of ZnO NPs. Also, the some of the important applications economically, medically and environmentally.

## 2. Procedure for the synthesis of zinc oxide nanoparticles (ZnO NPs)

Nanomaterials or nanostructures can be prepared with an assortment of methods, for example, physical synthesis, chemical synthesis and Biosynthesis. physical and chemical synthesis are an approach of synthesizing nanoparticles using miniaturized atomic components through self-assembly. Biosynthesis involve the synthesis of nanoparticles from microorganisms and plants that have biomedical applications. **Figure1** shows the major synthesis used for ZnO NPs<sup>28</sup>.

### 2.1. Chemical methods

Nanomaterials or nanostructures can be prepared by chemical methods with an assortment of technique, for example, Hydrothermal Technique, Vapor Transport, Precipitation Method, Self-Combustion technique, Sol-gel method and microemulsion method<sup>18</sup>.

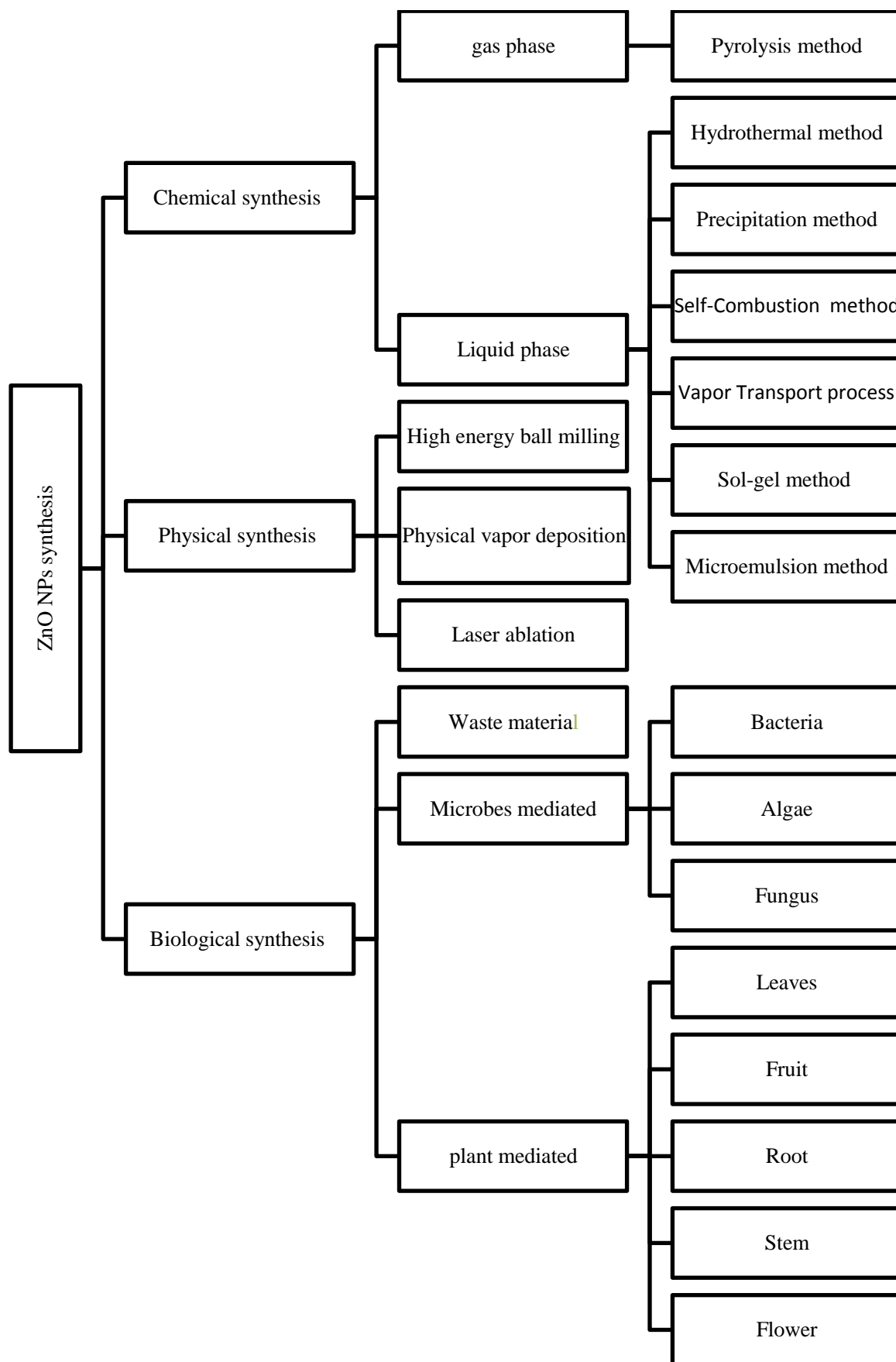


Figure 1 The major synthesis used for ZnO NPs

### 2.1.1. Hydrothermal method

Hydrothermal technique is a proficient alternative synthetic technique as a result of the low procedure temperature; it is much simpler to control the particle size. This procedure has some focal points, for example, easy equipment, ecofriendliness, catalyst-free growth, uniform generation, minimal cost, and being low risky over other growth processes. This strategy is plastic attractive and attractive one for microelectronics because of low reaction temperatures. This procedure has been effectively utilized for preparation of ZnO NPs and other luminescent materials. The size and molecule morphology can be controlled through the hydrothermal process by adjusting the reaction time, precursors concentration and temperature.<sup>25</sup>

For synthesis the ZnO NPs, was synthesis stock solutions of Zn  $(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.1 M), and 25 mL of NaOH (from 0.2 M to 0.5 M) solution synthesized in methanol is added with stirring to obtain the pH value of reactants in the range of 8 to 11. Then were moved these solutions into Teflon lined sealed +stainless steel autoclaves and kept up for 6 to 12 hours at different temperatures in the scope of 100–200°C under autogenous pressure. The white solid product will be washed with methanol, filtered, and dried in air in oven at 60°C. Then the characterization of samples by X-ray diffraction technique will be done to determine their structures.<sup>21</sup>

### 2.1.2. Vapor transport method

The vapor transport synthesis is the most common method for the preparation of Zinc oxide nanostructures. In this process, oxygen or oxygen mixture vapors and zinc are transported and react with each other resulting in formation of Zinc oxide nanostructures. There are numerous ways to produce Zn and oxygen vapor. Decomposition of Zinc oxide is an easier, simpler, and direct method, but it is limited to very high temperatures such as ~1400°C.

Another direct method involves heating of zinc powder under the flow of oxygen. It involves relative low growth temperature (500~700°C), but to obtain the desired ZnO nanostructures the ratio between the Zn vapor pressure and oxygen pressure must need to be closely controlled in order. It has been watched that the modification in this ratio gives a large variation in the morphology (size and geometry) of nanostructures<sup>19</sup>.

### 2.1.3. Precipitation method

In this method ZnO can be synthesized by using urea and zinc nitrate as precursors. 0.5 M (4.735 gm) zinc nitrate  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 50 mL of distilled water under stirring for 30 minutes. Prepared 1 M (3.002 gm) urea in 50 ml of distilled water under constant stirring for 30 minutes;

this urea solution acts as precipitating agent. This urea solution is added dropwise into zinc nitrate solution with strong stirring for 2 hours at 70°C. Finally precipitating solution turns whitish cloudy. This white product is centrifuged for 10 minutes at 8000 rpm and washed with distilled water for the removal of any absorbed ions or impurities if present. Calcination of the obtained yield will be done in air atmosphere for 3 hours at 500°C using muffle furnace<sup>37</sup>

#### 2.1.4. Self-Combustion method

In this test was used ZnO and Zn(NO<sub>3</sub>)<sub>6</sub>H<sub>2</sub>O, adding HNO<sub>3</sub> dissolved and stirred for 1 month was dissolved Zn(NO<sub>3</sub>)<sub>6</sub>H<sub>2</sub>O in ethylene glycol, stirred for 3 days and heated up till self-combustion occurred at 110°C. Then the samples were dried in the oven for 24 hours at 110°C and then crushing for 1 hour. The samples were heated up to 400°C for 1 hour after put it in a crucible. This heating temperature has been used by other investigators to obtain the nanorods morphology of zinc oxide materials. next the heating process, The ZnO samples were then crushed for 1 hour to get small particles<sup>35</sup>.

#### 2.1.5. Sol-gel method

synthesized ZnO NPs were by a new sol gel way as the next method. Added the 0.015 mol ZnSO<sub>4</sub>·7H<sub>2</sub>O (Merck) and 1.2 g diethylene glycol (Merck) to mixed solution of 300 mL distilled water and 10mL ethanol (99.7% Merck). To obtain the gel the mixture was stirred with a magnetic stirrer for 2 hours at 850°C. Then was dried the obtained gel at 220°C for 1 hour, then ground into a fine particle. To attain the required temperature, the temperature of the dried precursor powder was increased at the rate of 10C/min and then the sample was stayed at 5000°C for 3 hours to obtain the final yield (i.e., ZnO nanoparticles). The specification of the size, structure and optical properties of the as-synthesis and annealed<sup>16</sup>.

#### 2.1.6. Microemulsion method

ZnO NPs were prepared by a reverse microemulsion system formed from sodium bis (2-ethylhexyl) sulfosuccinate (Aerosol OT, or AOT): glycerol:n-heptane. The zinc precursor was zinc acetate dihydrate. The growth of zinc oxide NPs was completed by calcination of premature zinc glycerolate microemulsion result in air at 300, 400 and 500°C<sup>45</sup>. Spray pyrolysis is a physical way, which is size controllable, little cost, reproducible, fairly easy and continuous for production of several mixed metal oxides, nano metal oxides and metals on metal oxides<sup>29</sup>. compared with those from wet chemical ones, Powders synthesis by this technique, are fewer agglomerated with greater purity, extra crystalline and also have big specific surface areas<sup>17</sup>. Zinc acetate dehydrate Zn (CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O with 99.5% of purity was acquired from Aldrich Chemical Company. Were synthesis the predecessor from distilled water and above

zinc acetate. Then were added some drips of glacial acetic acid to stabilize the solution. The concentration of zinc acetate in precursor solution was chosen to be 5, 15, 20 and 25 wt% for getting the best concentration of starting material. Dry air was used to give the wanted pressure for atomizing the solutions and also was used it as the carrier gas for carrying precursor solutions into the nebulizer<sup>11</sup>.

#### **2.1.7. Pyrolysis method**

This method is an attractive for synthesis a more uniform size and composition of spherical particles as well as for multi-component materials because of its high-production rate<sup>24</sup>. In this method, LiNO<sub>3</sub> was used as a shield in the synthesis of ZnO NPs. In the first, 0.1 mol/l of zinc acetate dihydrate was dissolved in ultrapure water. Then, 0.5 mol/l of LiNO<sub>3</sub> was added to a precursor solution of zinc acetate dihydrate. Ultrasonic transducer was used to atomize and mist precursor solution. The mist was carried by a 1–5 l/m in nitrogen flow into a hot wall tubular reactor. The temperatures were from 430°C to 630°C. Finally, the product was washed and dried overnight<sup>32</sup>.

### **2.2. Physical methods**

Zinc oxide nanoparticles can be prepared by physical methods such as high-energy ball milling method, laser ablation method and Physical vapor deposition method.

#### **2.2.1. High-energy ball milling method**

Mechanical milling method has established to be simple and an effective method without involving high temperature treatment for the production of nanoparticles powders<sup>5</sup>. The commercially available ZnO powder has been milled (size was 0.6–1 μm and purity was 99.9%) using hardened steel balls for different times ranging from 2 to 50 hours. The ratio of the mixture was around 15:1 of steel balls and ZnO powders, respectively. The milled materials were used directly with no added milling media<sup>38</sup>.

#### **2.2.2. Laser ablation method**

ZnO NPs were executed through pulsed laser ablation of a pure Zn plate in aqueous solution or in the pure water of sodium dodecyl sulfate (SDS, 99.5%) surfactants with different concentrations from 0.0001 to 0.1 M. A zinc plate (99.99%) was fixed on the bracket in a glass vessel filled with 10 mL aqueous solution which was continuously stirred to separate the smoke like colloids above the metal plate. The first harmonic (1064 nm) of an Nd:YAG laser operated at 10 Hz with a pulse width of 10 ns was used for ablating the material. It has been used laser energy of 50 mJ with the output of the 1064-nm. A Scientech power meter monitors the output of the 1064-nm laser with the output of 70 mJ/pulse. The laser beam was focused to a spot of 2 mm in diameter using a lens with a focal length of 150 mm onto the metal plate,

and the solution gradually turned from brownish to yellow with the increase of ablation time due to the colloidal suspension of nanoparticles of ZnO. Most solutions became slightly turbid after the ablation. For the 0.01 M SDS solution, it was completely transparent and stable for more than 1 week without aggregation, and no obvious change of the corresponding optical spectrum was observed in 1 week after ablation, whereas the 0.05 M SDS solution was comparatively stable in 3 days. In other samples, there appear some floccules in several hours<sup>48</sup>.

### 2.2.3. Physical vapor deposition method

In this method ZnO nanowires can be synthesized by using NiO nanoparticles-deposited  $Al_2O_3$  substrates.  $Al_2O_3$  can be used because, it consists of grain structure. In a typical process, added ethanol and 0.1 M of nickel nitrate to the  $Al_2O_3$  substrate (10 mm × 5 mm). Then, NiO particles were evenly formed on the  $Al_2O_3$  substrate after drying the  $Al_2O_3$  substrate at 400 °C in air. The substrate was put on top of a quartz boat filled by metal zinc powders. After that, a quartz boat was insert into the quartz tube furnace. The furnace was heated to reaction temperature under rate 500 sccm of Ar flow to synthesize ZnO nanowires. ZnO nanowires was synthesized by physically vaporizing zinc source under Ar (99.99%) flow rate of 500 sccm at the temperature range of 450-600 °C for 60 min<sup>22</sup>.

## 2.3. Biological synthesis

Biosynthesis approach is an environment-friendly. It is an approach of synthesizing nanoparticles includes synthesis through fungi, plants, bacteria etc. Biosynthesis methods are used for the synthesis of ZnO NPs because of the least possible number of chemicals used that produces least amount of pollutants<sup>28</sup>.

### 2.3.1. Synthesis of ZnO NPs using plant extract

Parts of a plant such as leaves, roots, stem, fruits and seeds have been used for ZnO NPs synthesis because of phytochemicals that they produce. Plants are the most preferred sources because they lead to large-scale production and various in size and shape of nanoparticles. One of the most common ways to prepare ZnO NPs from leaves and flowers is to take part of the plant and wash it very well using tap water. double distilled water is then used as a final step. Double distilled water is then used as a final step. After that, left it at room temperature to dry. Then, the dried plant is grinded and weighed. Milli-Q H<sub>2</sub>O is added to the plant part according to the required concentration and boiling the mixture under continuous stirring<sup>13</sup> The solution is filtered using filter paper and adding 0.5 Mm of zinc oxide or hydrated Zinc nitrate to the plant extract. then, the mixture is boiling at the required temperature and required time<sup>36</sup>. Some perform optimization at this point using different pH, temperature, time and extract concentration. Incubation period results in a change of color of the mixture of yellow, which is a visual confirmation of

the synthesized nanoparticles. Then UV-Visible Diffuse Reflectance Spectroscopy (UV-DRS) is used to confirm the synthesis of nanoparticles followed by centrifugation of mixture and drying the pellet in a hot air oven to get the crystal nanoparticles<sup>44</sup>. **Table 1** shows the characteristics of ZnO NPs synthesized using some plants.

**Table 1** Some plants used in synthesis of ZnO NPs

Plant(family)	Part taken for extraction	Size(nm)	Shape	Functional group	References
<b>Aloe Vera (Liliaceae)</b>	Leaf extract	8–20 (XRD)	Spherical, oval, hexagonal	O-H of phenol, amines, O-H of alcohol and C-H of alkane, the amide of protein and enzymes.	3
<b>Trifolium Pratense (Legumes)</b>	Flower	60–70 (XRD)	Spherical	Hydroxyl,-C-O, -C-O-C, C=C stretching mode	7
<b>E. Crassipes (Pontederiaceae)</b>	Leaf extract	32–36 (SEM&TEM), 32 (XRD)	Spherical without aggregation	C-O and C=O of esters, hydroxyl, C-H stretching.	41

### 2.3.2. Synthesis of ZnO NPs using microbes mediated

Nanoparticles synthesis using microbes such as bacteria, fungus, Algae, etc., it has several disadvantages such as screening of microbes is a time consuming process. Also, there is no control on the size and shape of nanoparticles and also the cost used to bacterial growth is very high<sup>1</sup>.

Algae are a photosynthetic organism which ranges from the multicellular ones (ex.Brown algae) to the unicellular forms (ex.Chlorella). Algae has been used extensively for the synthesis of gold and silver nanoparticles but its application for synthesis of zinc oxide nanoparticles is limited and reported in a very less number of paper<sup>40</sup>.



Extracellular synthesis of nanoparticles from the fungus are helpful because, it widely used of production. It is preferable to use fungi more than bacteria because it has metal bioaccumulation property and metal bioaccumulation property.

ZnO NPs synthesis by adding different concentrations of zinc oxide to the microbe until white deposition starts to deposit at the bottom of flasks indicating initiation of transformation. This solution is then transformed into centrifuge tubes and centrifuged at 3000 rpm for 10-20 min to separate the synthesized ZnO NPs <sup>2</sup>. **Table 2** shows the characteristics of ZnO NPs synthesized using different type of microbes

**Table 2 some microbes used at synthesis of ZNO NPs**

Microbes type	Family	Size(nm)	Shape	Functional group	References
<b>Pseudomonas aeruginosa (bacteria)</b>	Pseudomonadaceae	35–80 (TEM), 27 (XRD), 81 (DLS)	Spherical	O-H stretching vibration, -CH of aliphatic stretching vibration, ester carbonyl group	39
<b>S. Myriocystum (algae)</b>	Sargassaceae	46.6 (DLS), 20–36 (AFM)	Spherical, radial, triangle, hexagonal, rod	O-H and C = O stretching band, carboxylic acid	26
<b>Aspergillus terreus (fungus)</b>	Trichocomaceae	54.8–82.6 (SEM), 29 (XRD)	Spherical	C-N bond of primary amine, C-O of primary alcohol, primary &	4

### 2.3.3. Synthesis of ZnO NPs using waste material

Many wastes such as slaughter goat waste (mainly intestine) and peels of fruit and vegetable were used to synthesize zinc oxide. When using slaughtered goat waste, the simple distillation method was adopted. Adding ethanol to slaughter goat waste, then boiling the solution with zinc chloride salt. Then conglomerates of ZnO NPs were produced. The size of it was 3–11 nm<sup>15</sup>. When using peels of fruit and vegetable, The distilled water was added to the powder of extract. the solution was stirred at 80 °C for 45 minutes. Then mixed with ZnO under constant stirring at 90 °C for 4 h. After this time, the temperature was reduced to 30°C with continuous stirring for 24 h. After that, the powdered annealing was carried out in a muffle furnace at 400°C for 1 h. The white powder was obtained<sup>7</sup>.

### **3. Applications of ZnO NPs**

ZnO NPs have many important applications economically, medically and environmentally. ZnO NPs have attracted intensive study efforts for their unique properties and many applications in ultraviolet light emitters, spin electronics, chemical sensors, piezoelectric devices, and transparent electronic, and it can be used as photocatalytic degradation materials of environmental pollutants. Big and thin films of ZnO have showed high sensibility for some harmful gases. At present recorded ZnO as a “generally recognized as safe (GRAS)” material by the Food and Drug Administration and furthermore utilized as a food additive. Zinc oxide nanostructures show great catalytic efficiency, and also the great adsorption ability, and are use as a part of the fabricate of sunscreens and another applications. In this research some of them will be mentioned<sup>9</sup>.

#### **3.1. Toxicity of ZnO NPs towards carcinogenic cells**

ZnO nanoparticles have antitumor activity against several types of cancer, such as human osteoblast cancer cells<sup>27</sup>, human colon carcinoma cells<sup>6</sup> and human myeloblastic leukemia cells<sup>34</sup>. Also, ZnO NPs have exhibited a preferential ability to kill human myeloblastic leukemia cells (HL60) compared to healthy eukaryotic cells (normal peripheral blood mononuclear cells)<sup>34</sup>.

#### **3.2. ZnO nanocomposites as antimicrobial food packaging**

ZnO NPs have activity against a wide range of microorganisms, and it have antimicrobial properties against foodborne pathogens by Pathogenic bacteria, viruses and toxins produced by microorganisms. So it can use for food preservation as antimicrobial food packaging. therefore, ensures the protection of the packaged food.<sup>9</sup>.

#### **3.3. Zinc oxide NPs in modern sunscreens**

Zinc oxide nanoparticles can be combined with sunscreens to provides broad protection against the known carcinogenic<sup>30</sup>. Because, it show the broadest UV protection more than other commercial sunscreens<sup>33</sup>.

#### 4. Conclusion

Physical and chemical synthesis are an approach of synthesizing nanoparticles using miniaturized atomic components through self-assembly. Biosynthesis involve the synthesis of nanoparticles from microorganisms and plants that have biomedical applications. The ZnO NPs can have large applications in the field of food, pharmaceutical, and chemical industries.

#### 5. Recommendations

The NPs synthesis from plants have Lots of applications in different fields such as, cosmetic industries, pharmaceutical and food. So the authors suggest that many studies should be done in this field.

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### ملخص الدراسة

أكسيد الزنك هو مركب غير عضوي يستخدم على نطاق واسع في التطبيقات اليومية. وقد أدى ظهور تكنولوجيا النانو إلى تطوير مواد تكون ذات خصائص جديدة لاستخدامها في كثير من التطبيقات. وهكذا أظهرت أكسيد الزنك في النانو خصائص مميزة وهامة. لذلك تم في هذا البحث مناقشة تحضير مركب نانو أكسيد الزنك بواسطة عدة طرق مختلفة تشمل أهم الطرق الفيزيائية والطرق الكيميائية والطرق الحيوية الأساسية كما تم ادراج بعض التطبيقات الهامة المعتمدة على مركب نانو أكسيد الزنك.

الكلمات المفتاحية: أكسيد الزنك، الطرق الحيوية، أكسيد المعادن؛ الجزيئات النانوية.

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