Synthesis of Metallic Nanoparticles by Physical, Chemical and Biological Methods and Their Characterization

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Abstract

Nanoparticles are the particles ≥100 nm. They have diverse applications. Physical method is top down method. It is time consuming. Chemical method is simple, but expensive and requires expensive chemicals with high purity. Biological method is very simple, cheap and environment friendly requiring no expensive chemicals, temperature and is time saving. The plant or fungal extract can be used in this method. These are available anywhere. In present work we synthesized Zinc, Nickel and Chromium oxide nanoparticles by sol-gel method and biological method. We used fungal extract in which enzymes converted metal salts in to nanoparticles. These particles were characterized by XRD (X-ray Diffraction), EDX (Energy Dispersive X-Ray Spectroscopy), UV-Vis (Ultraviolet Visible) and SEM (Scanning Electron Microscopy). Their size was calculated. It was in nm range. The size of nanoparticles of ZnO, NiO and Cr₂O₃ was 47, 38 and 45 nm respectively. The use of these nanoparticles is versatile. ZnO NPs are used in cosmetics and in bioenergy production, as a catalyst and as antibacterial material. NiO nanoparticles have potential applications in electronics, magnetism, energy technologies and in nanomedicines. The Cr₂O₃ nanoparticles are used in wear resistant materials, pigments and solar energy collectors.

Key Words: Nanoparticles, Sol-Gel method, Biological method, Chromium oxide nanoparticles, Scanning Electron Microscopy.

1-Introduction

Nanotechnology is the engineering of individual atoms and molecules with dimensions of less than 100 nm [1]. Idea of nanotechnology was given by Richard Feynman and this term was used in scientific fields in 1974 [2]. Nanoparticles have outstanding physicochemical properties. Nanoparticles have various applications in catalysis, electronic devices, dyes and pigments [3,4]. When size of the particles becomes less than 70 nm, Van der Waals force is
developed. Gecko can climb the walls and walk on ceilings because of minute hairs on their limbs. Gold NPs change their ability to reflect light when their size is less than 20 nm. Al NPs are extremely reactive when their size is less than 20 nm. The fascinating aspect of nano is change in properties of particles when they are very small [5]. General procedures for metal nanoparticles synthesis are electrochemical method, thermal decomposition, electromagnetic irradiation, sol-gel method, chemical reduction, ultraviolet irradiation, aerosol technologies, lithography, laser ablation, photochemical reduction techniques, attrition and pyrolysis. Chemical methods have drawbacks of contamination by toxic solvents and production of hazardous byproducts. Biological methods using microorganisms are clean, nonhazardous, eco-friendly and energy efficient. These reduce metal ions at faster rate and are carried out at ambient conditions. Microorganisms can survive in difficult conditions such as high concentration of metals by adopting survival mechanisms such as efflux system, extracellular combination and precipitation and chemical detoxification. According to Beveridge efflux system, alternation of solubility and toxicity by reduction, biosorption, bioaccumulation and lack of specific metal transportation system are the mechanisms responsible for biosynthesis [6,7].

Zinc oxide (ZnO) is considered magic material because of its unique properties and vast range of applications [8]. Precipitation method was used for ZnO NPs synthesis using Zn(NO$_3$)$_2$·6H$_2$O as a precursor and Potassium carbonate as a precipitator [9]. The ZnO NPs can be prepared by Biological methods using leaf extract of Coriandrum sativum, Acaphyla indica, milky latex of Calotropis procera and Arya sativa [10]. Trifolium pretense flower extract and fruit extract of Rosa canina is also used for the synthesis of ZnO NPs [11]. Zinc oxide NPs are used in biomedicine like biomedical imaging, drug delivery, gene delivery, and bio sensing [12]. Various techniques have been developed to synthesize Cr$_2$O$_3$ nanoparticles. Chromium oxide nanoparticles can be synthesized by aqueous precipitation method using ammonia as a precipitating agent and Cr$_2$(SO$_4$)$_3$ as a precursor. Gibot and L.Vidal prepared Cr$_2$O$_3$ NPs by the thermal decomposition of Cr(NO$_3$)$_3$·9H$_2$O at 550°C [13]. Kohli et al prepared Cr$_2$O$_3$ NPs by a precipitation method.V.S.Jaswal et al used precipitation method for synthesis of Cr$_2$O$_3$ NPs by reacting Cr$_2$(SO$_4$)$_3$ and aqueous ammonia [14]. The Cr$_2$O$_3$ nanoparticles are also synthesized biologically by the reduction of potassium dichromate solution with Mukia Maderaspatana plant extract [15]. Chromium oxide nanoparticles have vast domain of applications in optical and electronic devices, as catalysts, colorants, hydrogen storage coatings and wear resistance materials [16]. Nickel oxide NPs have fascinating properties like anodic electrochromism,
excellent durability, electrochemical stability and large spin optical density. Variety of methods are used for the production of Nickel Nanoparticles. Nickel nanoparticles were synthesized by chemical reduction method using nickel chloride hex hydrate as a precursor and polyvinylpyridilidone (PVP) as a capping agent. Nickel nanoparticles are also synthesized by solution reduction process using acetonitrile as a solvent, benzildiethylenetriamine as a reducing agent and nickel nitrate hex hydrate as a precursor [17]. The dead biomass of fungus Hypocrea lixii was used as an ecofriendly method for nickel NPs synthesis through biosorption [18]. Nickel Oxide NPs have extensive applications such as catalysis, battery cathodes, gas sensors, electro chromic films, dye sensitized photocathode and magnetic materials [19].

1.1-Experimental

In present study we synthesized ZnO, Cr2O3 and NiO NPs by using Chemical and biological methods. This study was carried out at Nanoscience & Technology Department, National Centre for Physics, QAU Islamabad and Department of Chemistry, University of Wah, Wah Cantt. These nanoparticles were synthesized by sol-gel technique and were characterized by using X-ray diffraction, UV-Visible spectroscopy, Scanning Electron Microscopy and Electron Dispersive X-ray Spectroscopy. During this work all chemicals were purchased from local market of Sigma-Aldrich. These were AR-Grade and there was no need of further purification. The Chemicals used were Zinc chloride (ZnCl2), chromic sulfate (Cr2(SO4)3), nickel nitrate Ni(NO3)2 and sodium hydroxide. We used deionized water throughout the experiment.

1.1.1. Chemical Synthesis

In this method aqueous solutions of salts were prepared by dissolving 3-4 g of nickel, chromium and zinc salts in 100 ml of deionized water. We stirred the solutions to dissolve the salts completely. We titrated salt solutions by adding 0.5M NaOH drop wise from burette with vigorous stirring. Frequently we checked the pH. The precipitates were formed when pH was 11. The colour of precipitates of zinc was pale white while that of nickel and chromium was blue green and green respectively. These precipitates were washed 4-5 times with de-ionized water and then were dried at 95°C to remove moisture. Dried precipitates were calcined at 550°C for three hours in a muffle furnace. The calcined material was grinded by mortar and pestil and samples were prepared. These samples were characterized by analytical techniques like XRD, SEM, UV-Vis and EDX.
1.1.2. Biological Synthesis

In this method first of all salt solution was prepared by dissolving 3-4 g of salt in deionized water and mixed with 2 g crushed powder of Aspargillus niger and stirred for 30 minutes. Then the resultant material was placed in dark for 3 days. After 3 days we filtered the solution. The filtrate was characterized by UV-Visible for finding size and concentration of nanoparticles. The filtrate was then dried and calcined in furnace at 550°C for 3 hours. Now the material was grinded and analyzed by XRD, SEM and EDX.

We analyzed nanoparticles by using XRD model D8 ADVANCE BRUKER X-Source Copper/(anode). UV-Vis was performed on UV-Vis Spectrometer Perkin Elmer, Lambda 25. Both instruments were placed at Nanoscience & Technology Department, QAU Islamabad. The Scherrer formula was used for finding size. All the samples were characterized by XRD and their results were noted in nanometer. The synthesized NPs were also characterized by SEM performed on SEM, TESCAN, VEGA3 placed at Advanced Energy & Material lab NUST. The SEM study was carried out to find size and morphology of nanoparticles. The EDX was done on EDX Oxford placed at Fracture Mechanics and Fatigue Lab, Mechanical Engineering Department, UET Taxila. The EDX was used to find elemental composition and purity of samples.

1.1.3. Results and Discussions

We characterized samples by XRD. The XRD was used to find size of particles and crystallinity. The scherrer formula was used to find crystalline size of NPs. The XRD analysis of biologically synthesized nanoparticles is described below.

![XRD Spectrum of ZnO NPs](image)

Figure 1- The XRD spectrum of ZnO NPs

The above XRD pattern of ZnO nanoparticles indicates that the peaks are sharp and are located at 2θ values of 31°, 34°, 36°, 38°, 47°, 56°, 62° and 69°. Sharp peaks show good crystalline growth and the position of peaks at respective 2θ values indicate the formation of pure ZnO nanoparticles. These results were matched with (Arora et al., 2014), (Farahmandjou and Jurablu, 2014) and (Zargar and Arora, 2017).
Table 1 XRD data of ZnO NPs

<table>
<thead>
<tr>
<th>S.NO</th>
<th>PEAKS</th>
<th>POSITION OF PEAKS</th>
<th>PARTICLE SIZE</th>
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<tr>
<td>1</td>
<td>1</td>
<td>31</td>
<td>47nm</td>
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<tr>
<td>2</td>
<td>2</td>
<td>34</td>
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<td>3</td>
<td>3</td>
<td>36</td>
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Average particle size found for ZnO NPs according to positions of XRD peaks was 47 nm.

Figure 2 - The XRD spectrum of NiO NPs

The diffraction peaks for NiO nanoparticles were at 19°, 28°, 29°, 32°, 34°, 37°, 43°, 49°, 54° and 63° which were matched with (Vasudeo and Pramod, 2016) and (Sudhasree et al., 2014). Peaks were sharp and prominent representing formation of NiO NPs. The peaks line width described nanoparticle nature of sample.

<table>
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<tr>
<th>S.NO</th>
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<th>POSITION OF PEAKS</th>
<th>PARTICLE SIZE</th>
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<td>1</td>
<td>1</td>
<td>19</td>
<td>38nm</td>
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<td>2</td>
<td>28</td>
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<tr>
<td>3</td>
<td>3</td>
<td>29</td>
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<tr>
<td>4</td>
<td>4</td>
<td>32</td>
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Average particle size for NiO NPs was found to be 38 nm according to the XRD data plotted in table 2.

The peaks for chromium oxide NPs were formed at 2θ values of 24°, 33°, 36°, 41°, 50°, 54°, 63° and 65°. These results were matched with (Kalantari and Olayai, 2015). The peaks were sharp and clearly distinguishable. All the peak positions and intensity of peaks indicate crystalline Cr₂O₃ NPs.

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<th>S.NO</th>
<th>PEAKS</th>
<th>POSITION OF PEAKS</th>
<th>PARTICLE SIZE</th>
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<td>1</td>
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<td>24</td>
<td>45nm</td>
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<td>33</td>
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The XRD data for Cr$_2$O$_3$ nanoparticles shows that the average particle size was 45 nm. Chemically synthesized nanoparticles of nickel, chromium and zinc show diffraction peaks at $19^\circ, 24^\circ, 28^\circ, 33^\circ, 36^\circ, 41^\circ, 46^\circ, 54^\circ, 31^\circ, 34^\circ, 36^\circ, 47^\circ, 56^\circ$ respectively.

The EDX study showed the elements Zn and O. The Zn content was 85.9% while O content was 8.6%. The EDX results indicated that ZnO NPs were pure with only traces of impurities.

Elemental analysis of NiO NPs demonstrated that synthesized NiO NPs consisted of 53.8% Ni content and 46.2% O content without any trace of other materials.
The EDX analysis confirmed the presence of Cr$_2$O$_3$ NPs. It showed 61% Cr$_2$O$_3$, 38.8% O and 0.2% S.

SEM is used to study surface morphology of NPs by scanning the surface with high energy electrons. SEM study shows that Cr$_2$O$_3$ NPs are beautiful white hexagonal crystals. All the crystals are uniform sized with average crystalline size of 73 nm. There were very fine particles detected but because of their instability we could not find their exact size.
Figure 8 - The SEM Micrographs of NiO NPs

SEM study of NiO NPs showed spherical black uniform sized nanoparticles with average size of 47 nm which is very near to its XRD size of 45 nm. There was agglomeration noted at different locations.

Figure 9 - The SEM Micrographs of ZnO NPs

The SEM micrographs of ZnO NPs clearly show beautiful white evenly sized crystals with hexagonal morphology. The average size of crystals was 72 nm. Intense agglomeration in case of ZnO NPs is due to large surface energy of NPs.
The UV-Visible analysis was recorded in the range of 200-800 nm. The UV-Visible analysis indicates that ZnO NPs show maximum absorbance at 350 nm due to SPR, which occurs due to resonance of collective conduction electrons with incident electromagnetic radiations. The value was matched with the literature where values of maximum absorbance were between 340-380 nm.

NiO NPs show wide absorbance in the range of 220-350 nm. Wide absorbance represents wide size distribution of nanoparticles.
Chromium oxide NPs showed exciton absorbance around 430 nm which was matched with the literature. The second peak at around 580 nm is may be due to the presence of impurities or transition state.

2. Conclusion

The present study shows that Nickel oxide, Zinc oxide and Chromium oxide NPs were successfully synthesized by chemical and biological methods. The XRD study shows that the size of zinc, nickel and chromium NPs synthesized by biological method was 47, 38 and 45 nm respectively. The size of Biologically Synthesized nickel oxide, chromium oxide and zinc oxide NPs was 36.6, 37.4 and 40.8 nm respectively. The SEM study shows that ZnO and Cr$_2$O$_3$ NPs are hexagonal while NiO NPs have spherical morphology. The EDX shows that synthesized nanoparticles are pure and there is only trace of impurities present in the samples. Chromium oxide NPs have applications in the stropping knives, glasses, inks, paints and precursor to the magnetic pigment. Nickel oxide NPs are used as catalysts, battery cathodes and gas sensors. The ZnO is used in ceramics, glass, cement, ointments, paints and lubricants, adhesives, plastics, pigments, batteries and fire retarders.

3- Acknowledgement

We acknowledge the provision of services of NS & TD, NCP, QAU Islamabad.

4- References


