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Effect of Azadirachta Indica in Metal Oxide Nanoparticles

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Abstract

Nanotechnology has come to mean a range of highly promising disciplines in science and technology. Metal oxide Nanoparticles had been used in recent studies due to its large bandwidth and high binding energy and it has potential applications like antibacterial, antifungal, anti-diabetic, anti-inflammatory, wound healing, anti-oxidant and optic properties. The usages of nanomaterials are enormous as energy storage devices such as fuel cells, detection of threads in defence, navy, drug delivery and water purification. Green synthesis of Nanoparticles has received a lot of attention and close scrutiny of scientists and researchers. Leaf extract of Azadirachta Indica contains phytochemicals and enzymes which take part in the conversion of metal compounds into Nanoparticles. Pure zinc oxide and Manganese oxide is prepared and doped with Azadirachta Indica to analyse its general and optical properties. We have attempted to prepare pure ZnO and MnO Nanoparticles also both were doped with neem at 5:1 ratio by using solvothermal method.

Keywords: ZnO Nanoparticles ,MnO Nanoparticles ,Azadirachta Indica, XRD Analysis ,UV Analysis

1. Introduction

Nanoscience is the study of systems in nanoscale and nanotechnology is ability to systematically organize and manipulate properties and behavior of matter in the atomic and molecular levels. Nanotechnology is defined as the study and use of structure between1nm and 100 nm in size. It can detect sensors to detect very small amounts of chemical vapors. Various types of detecting elements, such as carbon nanotubes, zinc oxide nanowires or palladium nanoparticles can be used in nanotechnology based sensors. Nanotechnology, which deals with devices typically less than 100 nm in size, is expected to make a significant contribution to the fields of computer storage, semiconductors, biotechnology and energy.

Nanotechnology is the creation of useful or functional materials, devices and systems through control of matter on the nanometer length scale and exploitation of novel phenomena and properties which arise because of the nanometer length scale. Nanotechnology includes the synthesis, characterization, exploration and utilization of nanostructured materials. The nanostructured materials are very interesting materials both for scientific reasons and practical applications [6]

The eco-friendly approach of metal and metal oxide nanoparticles synthesis is a newer method without causing harm to the environment by avoiding the use of harsh, toxic, hazardous chemicals [1-3]. Leaf extract of Azadirachta Indica contains phytochemicals and enzymes which take part in the conversion of metal compounds into nanoparticles [3-5]. The phytochemicals present in neem leaf extract acting as bioreductant are flavones, organic acids, ketones, amides and aldehydes out of which flavones and organic acids are water-soluble phytochemicals that are responsible for the responsible of zinc ions into zinc nanoparticles.

1.1 Zinc oxide nanoparticles

Nanoparticles of zinc oxide (ZnO) that have diameters less than 100 nanometers. They have a large surface area relative to their size and high catalytic activity. The exact physical and chemical properties of zinc oxide nanoparticles depend on the different ways they are synthesized. Some possible ways to produce ZnO nano-particles are laser-ablation, hydrothermal methods, electrochemical depositions, sol–gel method, chemical vapour deposition, thermal decomposition, combustion methods, ultrasound, microwave-assisted combustion method, two-step mechanochemical–thermal synthesis, anodization, co-precipitation, electrophoretic deposition, and precipitation processes using solution concentration, pH, and washing medium.

1.2 MnO Nanoparticles

Manganese oxide is an inorganic compound with chemical formula MnO. It forms green crystal or powder. The compound is produced on a large scale as a component of fertilizers and food additives. Manganese oxide minerals have been used for thousands of years—by the ancients for pigments and to clarify glass, and today as ores of Manganese metal, catalysts, and battery material. More than 30 Manganese oxide minerals occur in a wide variety of geological settings. They are major components of Manganese nodules that pave huge areas of the ocean floor and bottoms of many fresh-water lakes. Manganese oxide minerals are ubiquitous in soils and sediments and participate in a variety of chemical reactions that affect groundwater and bulk soil composition. Their typical occurrence as fine-grained mixtures makes it difficult to study their atomic structures and crystal chemistries.

1.3 Green synthesis of Nanoparticles:

Green synthesis of Nanoparticles aims at minimizing generated waste and implementing sustainable processes. In recent years, green processes using mild reaction conditions and nontoxic precursors have been emphasized in the development of nanotechnology for promoting environmental sustainability.

The biological method, which is represented as an alternative to chemical and physical methods, provides an environmentally friendly way of synthesizing nanoparticles. Moreover, this method does not require expensive, harmful and toxic chemicals. Metallic nanoparticles with various shapes, sizes, contents and physicochemical properties can be synthesized. Synthesis can be done in one step using biological organisms such as bacteria, antibacterial, yeasts, molds, algae and plants, or their products.

Molecules in plants and microorganisms, such as proteins, enzymes, phenolic compounds, amines, alkaloids and pigments perform nanoparticle synthesis by reduction. In traditional chemical and physical methods; reducing agents involved in the reduction of metal ions and stabilizing agents used to prevent undesired agglomeration of the produced nanoparticles carry a risk of toxicity to the environment and to the cell. Besides, the contents of the produced nanoparticles are thought to be toxic in terms of shape, size and surface chemistry. In the green synthesis method in which nanoparticles with biocompatibility are produced, these agents are naturally present in the employed biological organisms. Below figure summarizes how nanoparticles are produced by biological methods. Because of rapid development, affordable culturing costs and easy control and manipulation of growth environment, bacteria are clearly targets in the production of Nanoparticles.

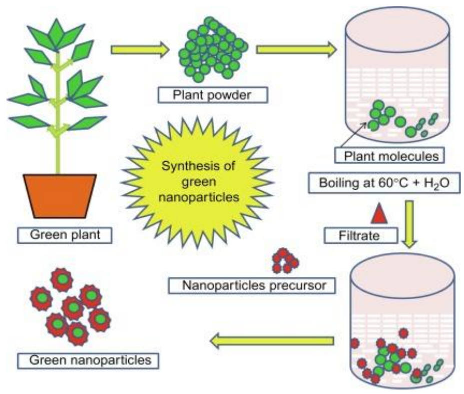

Fig.1. Green Synthesis

1.4 Use of plant extracts in nano particle synthesis:

The production of Nanoparticles using plant extract is alternative to the conventional methods, the photo synthesis is a green and eco-friendly technology used for production of large scale Nanoparticles. Plant extracts may act both as reducing agents and stabilizing agents in the synthesis of nanoparticles [6-9]. For nanoparticle synthesis mediated by plant leaf extract, the extract is mixed with metal precursor solutions at different reaction conditions. The parameters determining the conditions of the plant leaf extract (such as types of phytochemicals, phytochemical concentration, metal salt concentration, pH, and temperature) are admitted to control the rate of nanoparticle formation as well as their yield and stability. The phytochemicals present in plant leaf extracts have uncanny potential to reduce metal ions in a much shorter time as compared to fungi and bacteria, which demands the longer incubation time. Therefore, plant leaf extracts are considered to be an excellent and benign source for metal as well as metal oxide nanoparticle synthesis. Additionally, plant leaf extract plays a dual role by acting as both reducing and stabilizing agents in nanoparticles synthesis process to facilitate nanoparticles synthesis. The composition of the plant leaf extract is also an important factor in nanoparticle synthesis, for example different plants comprise varying concentration levels of phytochemicals [10-13].

1.5 Present study:

In the present study pure MnO nanoparticles and MnO added with neem extract and similarly ZnO nanoparticles and ZnO added with neem extractwere synthesized by using Solvothermal method and its general and optical properties are analysed. we have attempted to prepare 6 samples, pure MnO and pure ZnO, other MnOand ZnO mixed with neem leaf extract in different concentrations (2 ml and 5 ml). The prepared 6 samples were characterized using an automated X-ray diffractometer and their particle sizes were estimated by Debye-Scherrer method. UV-Vis-NIR spectra of all the prepared samples were also recorded using UV spectrophotometer and their optical band gap energy was also found out.

2. Materials and Methods

2.1 Plant Material:

Azadirachta Indica, commonly known as neem, nimtree or Indian lilac. Neem is a tree in the mahogany family sex Meliaceae. It grows in tropical and semi-tropical regions. The botanical name of neem is Azadirachta Indica.

2.2 Collection and Preparation of leaf extract:

Fresh and young greenish leaves were collected from Neem tree in the red clay soil in the area of Nagercoil, Kanyakumari district, Tamilnadu. The surface of the leaves was washed thoroughly for removing dust particles using distilled water for about 3 times. Each of these leaves were completely wiped with white colour Khadhi cloth and dried at room temperature. Then the weight of the leaf was measured. The weighed leaves were cut as tiny pieces, grinded which were mixed with 50ml of distilled water. The obtained solution was filtered separately in a clean beaker using Whatmann filter paper.

2.3 Preparation of pure manganese oxide and zinc oxide Nanomaterials:

Manganese acetate was stirred in distilled water until it gets soluble. Then NaOH was stirred in distilled water it gets soluble. Later NaOH is added drop by drop to the manganese acetate solution. After the above process, a gel like solution was formed and the precipitate was allowed to settle down. The resultant obtained was washed with distilled water and allowed to dry. After drying it was again washed with acetone to remove the impurities. The pure MnO sample thus prepared was subjected to various studies. Similarly, zinc acetate was used in same manner to prepare zinc oxide sample.

2.4 Addition of dopants:

The Azadirachta indica extract was added to the pure manganese oxide and zinc oxide in 2 different concentrations 2 ml and 5 ml. The prepared solution was heated in oven for 30mints allowed to settle, after a minute the settled precipitate was washed with distilled water and was allowed to dry for a week. After a week, the dried sample was again washed with acetone to remove impurities for three to four times and made to dry. The prepared samples were subjected to various studies.

3. Results and Discussion

The results obtained in the present study are reported and discussed here in this chapter.

3.1 General properties: XRD Analysis

All the prepared samples are in powder form whereas pure MnO is pale brown color, Azadirachta indica dispersion changes the color from pale brown to pale black color. Pure ZnO is white in colour,Azadirachta indica dispersion changes the color from white to pale white color. Such a color transition is often indicative of changes in the metal oxidation. The prepared samples were subjected to X-ray diffraction analysis. Variation of the lattice constants and crystallite sizes were obtained from the analysis of the observed XRD data shift to laser angles due to increase in lattice volume which is caused by the incorporation of dopant. All marked diffraction peak positions are in good agreement with the standard JCPDS data. The X-ray diffraction peaks at (1,1,1), (2,2,0), (2,2,1) planes confirm the formation of wurtzite structure of zinc oxide and (3,0,1), (2,1,0) and (2,0,0) planes confirm the formation of orthorhombic structure of manganese oxide. Using Debye-Scherer's equation the crystallite size of prepared samples was found.

Table.1. Crystalline size of the prepared samples

Samples	Crystalline size
Pure ZnO	16.35
2ml Azadirachta indica extract added ZnO	22.73
5ml Azadirachta indica extract added ZnO	24.5
Pure MnO	18.98
2ml Azadirachta indica extract added MnO	19.78
5ml Azadirachta indica extract added MnO	20.71

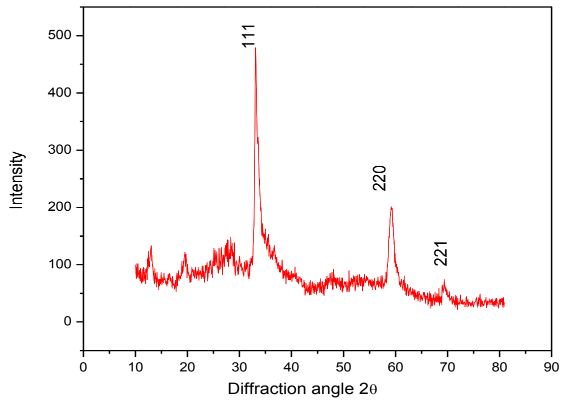

Fig.2.PXRD pattern for pure zinc oxide

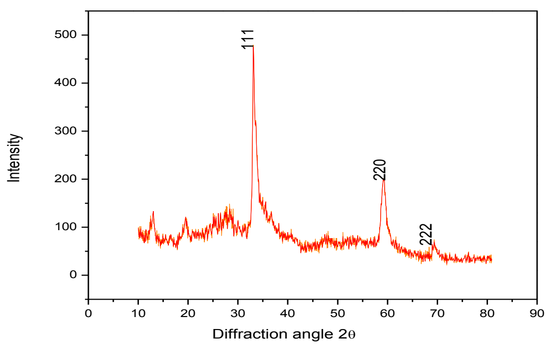

Fig.3. PXRD for 2 ml Azadirachta indicaextract added ZnO

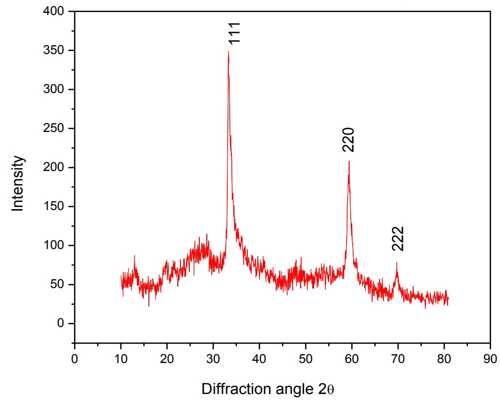

Fig.4. PXRD for 5 ml Azadirachta indicaextract added ZnO

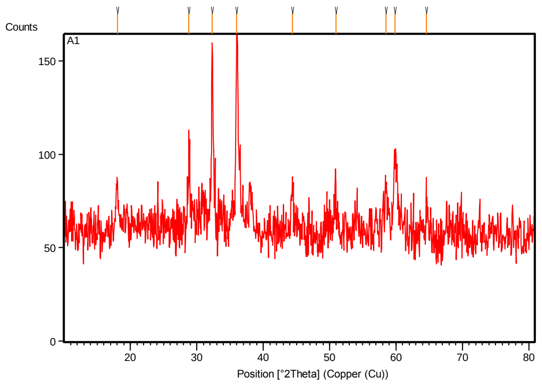

Fig.5. PXRD pattern for pure Manganese oxide

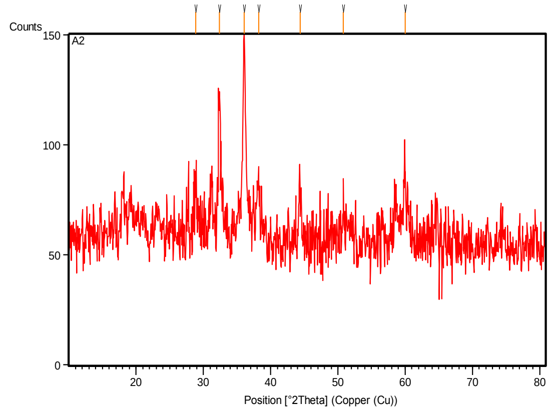

Fig.6. PXRD for 2 ml Azadirachta indicaextract added MnO

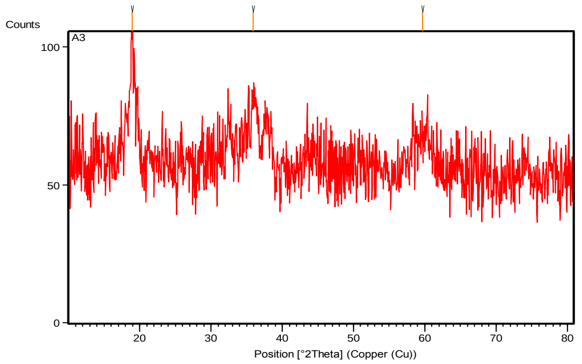

Fig.7. PXRD pattern for 5 ml Azadirachta indica extract added MnO

3.2 Optical Properties:

UV-Vis NIR Analysis

The structural studies show the quality of the material growth and also reflect the small yet distant changes in the crystal lattice that are likely to have an impact on the optical properties. We have investigated the change in absorption. The optical band gap observed for pure MnO and Azadirachta indica extract added MnO is comparable with that reported in the literature. The band gap of pure Manganese oxide is 4.15eV and the band gap of Azadirachta indica extract added MnO with concentrations of 2ml and 5 ml decreases from that of pure MnO. The ultraviolet absorption for the prepared samples is analysis of the observed UV varies from 5ev to 3ev for ZnO nps. The crystallite size increases and the energy band gap will get decreases for ZnO nps.The pure ZnO has remarkable absorption on ultraviolet region above 250nm wavelength whereas the Azadirachta Indica doped ZnO nanoparticles extend the absorption spectrum in uv-region.

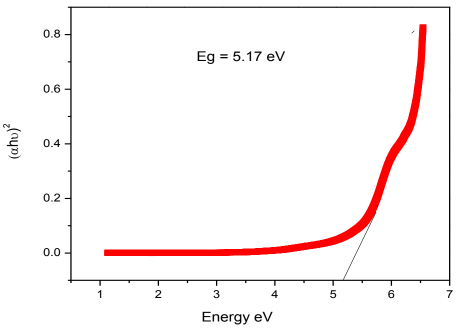

Fig.8.Energy band gap for pure zinc oxide

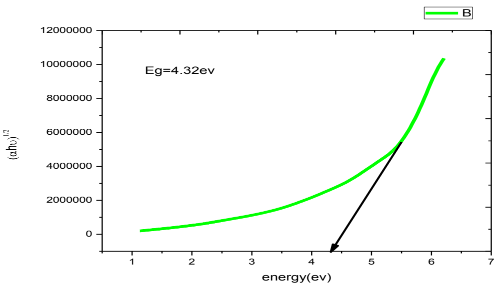

Fig.9. PXRD for 2 ml Azadirachta indicaextract added ZnO

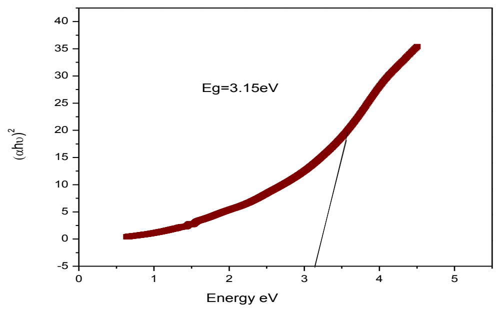

Fig.10.PXRD for 5 ml Azadirachta indicaextract added ZnO

The energy band gap of pure and Azadirachta indica added zinc oxide were found and tabulated in the below table.

Table.2.Energy band gap

Samples	Energy band gap
Pure ZnO	5.17 eV
2ml Azadirachta indica extract added ZnO	4.32 eV
5ml Azadirachta indica extract added ZnO	3.15 eV

The absorbance of the pure ZnO nanomaterials measured in the energy band gap is 5.17eV and the absorbance of the 2ml and 5ml Azadirachta indica mixed ZnO Nanoparticles energy band gaps are 4.32eV and 3.15 eV respectively. The optical band energies were calculated using Tauc plots. When the crystallite size increases, the band gap decreases.

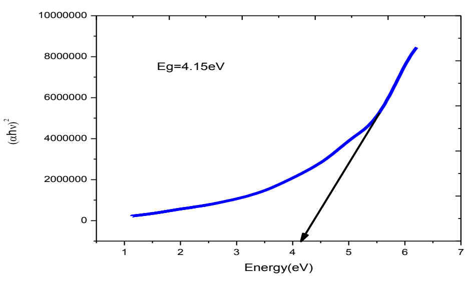

Fig.11.Energy band for pure Manganese oxide

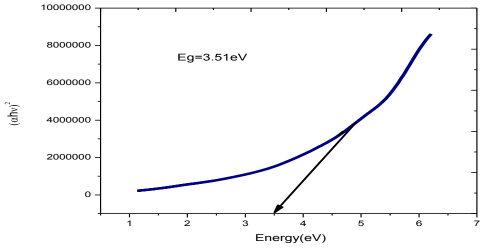

Fig.12. Energy Band Gap for 2ml Azadirachta indica extract added MnO

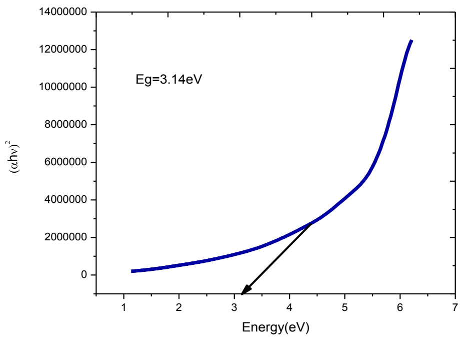

Fig.13. Energy Band Gap for 5 ml Azadirachta indicaextract added MnO

The energy band gap of pure and Azadirachta indica added Manganese oxide were found and tabulated in the below table.

Table.3. Energy band gap

Samples	Energy band gap
Pure MnO	4.15 eV
2ml Azadirachta indica extract added MnO	3.51 eV
5ml Azadirachta indica extract added MnO	3.14 eV

The absorbance of the pure MnO nanomaterial measured in the energy band gap is 4.15eV and the absorbance of the 2ml and 5ml Azadirachta indica mixed MnO nanoparticles energy band gaps are 3.51eV and 3.14 eV respectively. The optical band energies were calculated using Tauc plots. When the crystallite size increases, the band gap decreases. When the band gap decreases it results in the increase in electrical conductivity.

Summary and Conclusion

Nanotechnology has become dominant player in the scientific area. For the environment and energy, nanotechnology will have a significant impact. Green synthesizing nanomaterials become a powder field with so many truthful results in nanoscience and nanotechnology. Nano sized metal oxide has majority of practical uses. Also the use of plant materials has been considered a green route and a reliable method for the synthesis of nanoparticles owing to its environmental friendly nature. Hence an attempt has been made to synthesize the Zinc Oxide and Manganese oxide nanoparticles using aqueous neem (Azadirachta Indica) leaf extract by Solvothermal method. The aqueous leaf extract acts as a solvent with manifold roles as promoter, stabilizer and template for the synthesis of nanoparticles.

The prepared samples were subjected to X-ray diffraction analysis. Variation of the lattice constants and crystalline sizes were obtained from the analysis of the observed XRD. The crystallite size varies from 16nm to 24 nm for ZnO and 18-20 nm for MnO. The structural studies show the quality of the material growth and also reflect the small yet distinct changes in the crystal lattice that are likely to have an impact on the optical property. The ultraviolet absorption for the prepared samples is analysis of the observed UV varies from 5 eV to 3 eV for ZnO and 4 eV to 3 eV for MnO. The optical band gap observed for the prepared samples are comparable with that reported in the literature. The crystallite size increases and the energy band gap will get decreases. ZnO nanomaterials have attracted tremendous interest in the fields of photo catalysis, sensors, solar cells, super capacitors etc. The performance of intrinsic ZnO is limited by several factors such as insufficient light absorption, poor charge transport and low conductivity. When the band gap decreases it results in the increase in electrical conductivity. For some applications, such as sensors, electro chromic devices, organic photovoltaics, organic light emitting diodes, and field effect transistors. One advantage of utilizing conjugated polymers for such technological applications is the ability to tune the material properties at the molecular level. The electron band gap is an important concept to understand many phenomena associated with the nanomaterials. Whenever there is an overlap of valence and conduction bands, the electrons can move across freely into the conduction band. Manganese oxide and zinc Oxide is cheap and safe. When compared to the other synthesis technique Green synthesis is cheap and environment friendly and so we have carried out this technique in the present study for preparing pure and Azadirachta indica extract added metal oxide nanomaterials with high nature, feature and other optical applications.

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