

RESEARCH SCHOLAR PROGRAM (2019-2020)

VPM's B.N.Bandodkar College of Science
(Autonomous), Thane

Title of project: A systematic review on applications of WO₃ nanoparticles for antibacterial activity

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Following content is the work assignment of Research Scholar Programme
Module – Submission of Report of RSP Project done under the guidance
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RSP Assignment :- **Report Submission**

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1. **Method of Deposition of Thin Film & Characterization Technique**

1.1 **Methods of Deposition of thin films:**

During the initial part of research project undertaken, we have studied detailed methodology for synthesis of nanoparticles using three most widely methods such as;

- a. Chemical bath deposition**
- b. Hydrothermal synthesis**
- c. Electrodeposition**

In detailed experimentation, we studied principles of deposition, effect of different preparative parameters such as pH, concentration and temperature on thin film formation, and setup required for technique.

1.2 **Characterization techniques:**

1. **TEM (Transmission electron microscope) :-**

Introduction:- TEM is a powerful microscope that uses a beam of electron to focus on a specimen producing a highly magnified detailed imaging of the specimen. It is a powerful tool for material science. The first TEM was demonstrated by **Max Knoll** and **Ernst Ruska**.

Principle:- The working principle of TEM is based on light microscope but light microscope uses light. The TEM uses an electron beam to focus on the specimen to produce an image. In TEM when electron illuminates the specimen, the resolution power increases the wavelength of electron transmission. As the wavelength of electron is about 0.005 nm which is very much small but with the use of TEM the better resolution can be achieved. Since the wavelength of electron are 100,000 times shorter than visible light the electron microscope ie, TEM have greater resolving power The TEM can achieve 0.2 nm and magnifications upto 2,000,000 X That's why TEM can be used to detail the internal structure of smallest particle.

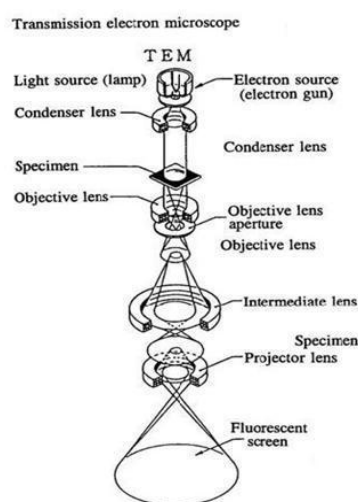


Fig 1

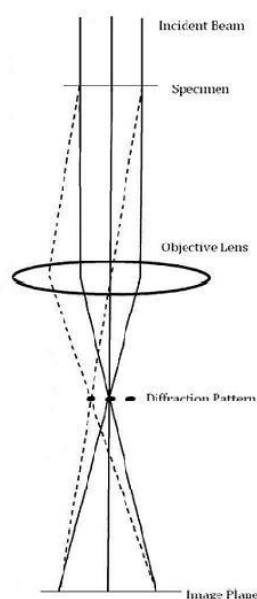
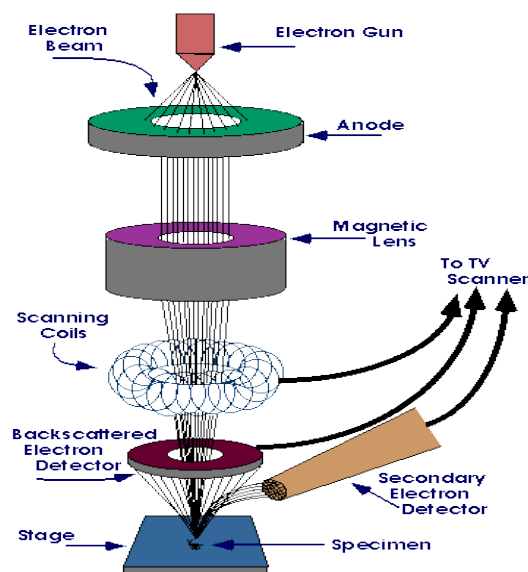


Fig 2

2. SEM (Scanning Electron Microscope) :-

Introduction :- SEM is a type of electron microscope that scans the surface. It uses a beam of electrons moving at low energy to focus and scan specimen. The first Scanning Electron Microscope was initially made by **Mafred von Ardenne**.



Principle:- It works on the principle of applying kinetic energy to produce signals on the interaction of electrons. These electrons are secondary electrons. The backscattered electrons and diffracted backscattered electrons which are used to view crystallized elements and photons. **Secondary and backscattered electrons** are used to produce an image. The secondary electrons are emitted from the specimen play the primary role of **detecting the morphology and topography of the specimen**. Backscattered electrons show contrast in the composition of the elements of the specimen.

3. XRD (X-ray powder diffraction) :-

Introduction :- X-ray powder diffraction is a rapid analytical techniques primarily used for phase identification of a crystalline material. It is now a common technique for the study of crystal structure and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample.

Principle :- X-ray are generated by a cathode Ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed towards the sample. Interaction of incident rays with sample produces constructive interference. when conditions satisfy the Bragg's law. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. Diffracted X rays detected. Conversion of diffraction peaks to d-spacing. Comparison of d-spacing with standard reference pattern. All diffraction method based on generation of X-rays in an X-ray tube. A key component of all diffraction is the angle between the incident and diffracted rays.

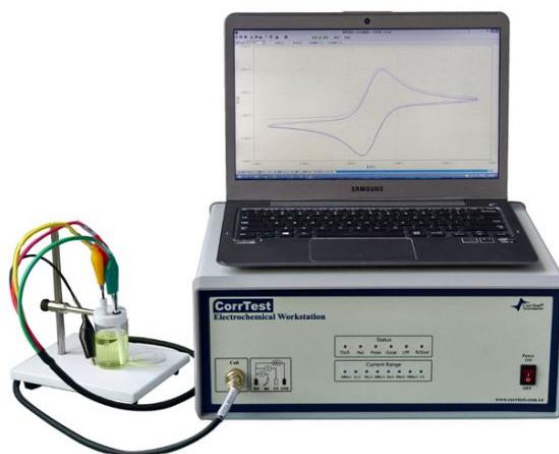
4. Cyclic Voltammetry (CV) :-

Introduction :- It is an electrochemical technique for measuring the current response of a redox active solution to a linearly cycled potential sweep between two or more set values. Cyclic Voltammetry uses a three electrode system consisting of

1. Working electrode. 2. Reference electrode. 3. Counter electrode.

CV is sophisticated potentiometric and voltammetric method. During a scan, the chemical either loses an electron (Oxidation) or gains electron (Reduction) depending on the direction of the ramping potential.

Principle:- It is based on the Nernst equation. It is performed by cycling the potential of a working electrode and measuring the resulting current. Here the current is measured while the potential between the two electrode is varied. The current generated is the result of electron transfer between the redox species and the electrodes. It is carried through the solution by the migration of ions. Here we measured and control the potential difference applied, as required for cyclic voltammetry, the potential of the working electrode is varied while the potential of reference electrode remains fixed.



5. Optical absorption techniques :-

It includes —

UV-Visible spectroscopy

I) Introduction :- It is a quantitative technique used to measure how much a chemical substance absorb light. It is done by measuring the intensity of light that passes through a sample with respect to the intensity of light through a reference sample or blank. It can be used for multiple samples including liquids, solids, thin films and glass.

II) Principle :- It is based on the absorption of ultraviolet light or visible light by chemical compounds which results in the production of distinct spectra. When matter absorbs the light it undergoes excitation and de-excitation resulting in the production of spectrum. When matter absorbs ultraviolet radiation, the electrons present in it undergoes excitation. It is important to note that the difference in the energies of the ground state and the excited state of the electron is always equal to the amount of ultraviolet radiation or visible radiation absorbed by it. The more easily excited electrons (ie, lower energy gap) the longer the wavelength of light it can absorb. ($\pi-\pi^*$, $n-\pi^*$, $\sigma-\sigma^*$, and $n-\sigma^*$) : These are the four possible types of transition. It can be ordered as follows: $\sigma-\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi^*$.

2. Nano materials used in Day-to-day Life

2. Products based on Nanomaterials used in day to day life

1. Sunscreen

Nanoparticles have been added to sunscreens for years to make them more effective.

Two particular types of nanoparticles commonly added to sunscreen are **Titanium dioxide and Zinc oxide**

These tiny particles are not only highly effective at blocking UV radiation, they also feel lighter on the skin



2. Clothing

When used in textiles, nanoparticles of silica can help to create fabrics that repel water and other liquids.

Silica can be added to fabrics either by being incorporated into the fabric's weave or sprayed onto the surface of the fabric to create a waterproof or stainproof coating.



3. Food Additives

Nano materials used : **Zinc oxide and Silica**

4. Solar panels

The Gratzel cell, which uses a layer of material coated with highly porous **Titanium dioxide** nanoparticles Which is less expensive to produce and allows cells to collect the sun's rays across a wider surface area.



5. **Mouthwash**

ZnO nanoparticles are commonly used in mouthwash. It act as anti bacterial agents.

6. **Bio aging of tumour cells**

Gold nanomaterials used for bio imaging of tumour cells.

7. **Bandages**

Bandages are normally applied to protect wounds from further contamination, but now studying new ways to enhance their antimicrobial properties using nanotechnology engineering.

Incorporating noble metals, which have natural antimicrobial properties, into bandages has been proven to help combat bacterial infections.

Silver disrupts the growth of bacteria by blocking its metabolism, engineers have developed ways to create bandages with silver nanoparticles woven into them.



8. **Concrete based products**

Addition of nanomaterials to cement-based materials, which can enhance their mechanical properties. Some such nanomaterials include **nano-silica (nano-SiO₂)**, **nano-alumina (nano-Al₂O₃)**, **nano-ferric oxide (nano-Fe₂O₃)**, **nano-titanium oxide (nano-TiO₂)**, **carbon nanotubes (CNTs)**. It improve the compressive, tensile and flexural strength of cement-based materials, as well as their water absorption and workability. The use of these nanomaterials can enhance the performance and life cycle of concrete infrastructures.



9. Transdermal patches

Transdermal patches typically deliver a specific dosage of medication after being placed onto a person's skin, allowing patients to avoid painful injections and gastrointestinal complications. Nanotechnology engineers are exploring ways that **microneedles** — small needles ranging in size (100-1,000 mm long) which can be incorporated into transdermal patches to solve this problem. The needles are affixed to a transdermal patch and painlessly penetrate the top layer of the user's skin.

10. Paints

The deterioration of both exterior and interior paints often occurs as a result of exposure to microorganisms. When microorganisms attack paint, the Paint surface is covered with a network of cells that can sometimes discolor the paint through their spore production, or by allowing for increased dirt retention.



Nano materials used in paint

i) Nanosilver :-

The high antimicrobial properties of both silver ions and nanosilver is attributed to the ability of this material to bind to bacteria cell proteins to induce cell death.

Nanosilver also showed to be far less toxic to the environment as compared to other popular paint biocides.

ii) Nano copper :-

Copper, as well as its nanoparticle form, induces cell death by the generation of reactive oxygen species (ROS), which is highly damaging to most biological molecules including DNA, protein and lipids.

Nanocopper exhibits effective antimicrobial activity.

3.**Literature Review on :-****a) WO_3 Thin Film for Anti-bacterial Activity**

In present detailed literature review, we performed literature search using standard methodology. Google scholar search engine was used to search different research articles. This study is restricted to literature study on WO_3 Thin Films for Anti-bacterial Activity during last five year (2015 onwards).

a) Thin Film for Anti-bacterial Activity:-

Thin films are layers of material deposited on a bulk substrate in order to impart properties that cannot be easily attained (or not attained at all) by the base material. It is a collective term that inhibit the growth of bacteria prevent the formation of microbial colonies and may destroy microorganisms. Many thin films were studied to show antibacterial activity.

Studies on Antibacterial activity are of great importance because many thin films responsible for elimination of several species of bacteria and to provide adequate protection against microorganisms.

Sr. No.	Name of Paper	DOI No.	Materials used	Techniques used	Conclusion
1.	Antibacterial, magnetic, optical and dielectric analysis of novel La ₂ O ₃ doped ZnO thin films	https://doi.org/10.1016/j.optmat.2020.110287	La ₂ O ₃ doped ZnO thin films.	Sol gel dip coating , XRD	La ₂ O ₃ doped ZnO thin films were synthesized and it was found that it shows strong antibacterial activity against <i>K. pneumonia</i> . bacterial strains. So, La ₂ O ₃ doped Zinc Oxide can be used to treat pneumonia.
2.	Surface and antibacterial properties of thin films based on collagen and thymol	https://doi.org/10.1016/j.mtcomm.2020.100949	Collagen & Thymol.	AFM	In this, surface and biological properties of collagen/ thymol materials were evaluated. Collagen Materials with Thymol addition inhibit dehydrogenase activity and decrease ATP level of tested pathogens. Results also suggest that collagen with thymol were helpful for preparation of wound dressing materials. Thus, it may still be considered in medical applications.
3.	Magnetic and antibacterial studies of sol-gel dip coated Ce doped TiO ₂ thin films: Influence of Ce contents	https://doi.org/10.1016/j.ceramint.2019.08.272	Ce doped TiO ₂ thin films.	SEM , XRD, Sol gel dip coating method	In this, Ce doped TiO ₂ thin films were prepared. It was also found that antimicrobial activity of Ce doped TiO ₂ is ineffective. Hence, doping of Ce can modify properties of TiO ₂ . It was also observed that during Ce doped TiO ₂ thin films, photoluminescence was detected which will be in future applications for LEDs & Solar Cells.

4.	Enhanced Photocatalytic and Antibacterial Ability of Cu-Doped Anatase TiO ₂ Thin Films: Theory and Experiment	https://dx.doi.org/10.1021/acsami.9b22056	Cu doped TiO ₂ thin films.	CVD, XRD, Raman spectroscopy, UV spectroscopy, XPS	It was observed that Cu doped TiO ₂ thin films shows antibacterial activity against (<i>E. coli</i> & <i>S. aureus</i>).
5.	Role of silver doping on the defects related photoluminescence and antibacterial behaviour of zinc oxide nanoparticles	http://dx.doi.org/10.1016/j.colsurfb.2017.07.071	Zinc Oxide Nanoparticles.	XPS	In this, the role of Ag doping and defects in ZnO NPs were studied for antibacterial and photoluminescence behaviour. The ZnO.Ag showed the several kinds of defects. These all were confirmed by XPS & XAS analysis. It was also investigated that undoped ZnO NPs showed strong antibacterial activity. While, ZnO.Ag NPs didn't show any antibacterial behaviour.
6.	Visible-Light-Responsive Antibacterial Property of Boron-Doped Titania Films	10.3390/catal10111349	Boron Doped Titanium Oxide Films.	XPS and XRD	It was found that TiO ₂ (B) thin films helps for control and elimination of human pathogens. TiO ₂ (B) thin films shows the visible light driven degradation and bactericidal effects without non photocatalytic antibacterial property of boron. The bactericidal effects induced by visible light are equally potent for elimination of model organism - <i>E. coli</i> and human pathogen - <i>Acinetobacter baumannii</i> , <i>Staphylococcus aureus</i> & <i>Streptococcus pyogenes</i> .
7.	Tungsten oxide. graphene oxide (WO ₃ . GO) nanocomposite as	https://doi.org/10.1016/j.jpccs.2018.01.021	Tungsten oxide. Graphene oxide	XRD	In this, several properties of prepared WO ₃ NPs & WO ₃ .GO NPs were studied. Antibacterial activity of WO ₃ .GO

	an efficient photocatalyst, antibacterial and anticancer agent		(WO ₃ .GO)		nanocomposite were investigated for <i>E. coli</i> & <i>Bacillus subtilis</i> . However, anticancer efficiency were also studied. It was found that WO ₃ .GO performs as a good antibacterial agent.
8.	Facile synthesis, characterisation of nano- tungsten trioxide decorated with silver nanoparticles and their antibacterial activity against water-borne gram negative pathogens	https://doi.org/10.1007/s13204-019-01186-z	Tungsten trioxide	EM (Electron microscopy)	Silver decorated tungsten trioxide metal oxide were synty using a facile wet impregnation technique. In this, it is found that this metal oxide is useful for inactivation of harmful water-borne gram negative pathogen. From EM, it was found that close contact of nano materials with bacterial cell wall caused cell death. With varying percentage of Ag with pure WO ₃ can be adapted for decontamination of drinking & wastewater content.
9.	Structural, Optical, and Antibacterial Efficacy of Pure and Zinc-Doped Copper Oxide Against Pathogenic Bacteria	https://doi.org/10.3390/nano1020451	Zinc doped copper oxide.	Hydrothermal technique	It was found that anti bacterial properties obtained in Zinc doped copper oxide against Gram negative (<i>Pseudomonas aeruginosa</i> , <i>Klebsiella pneumonia</i> , <i>Escherichia coli</i>) and Gram positive (<i>Staphylococcus aureus</i>) It was found that Zn doped are found to have more bacterial resistance than pure CuO.
10.	Low- cost green recyclable biomaterial for energy- dependent electrical switching and intact biofilm with antibacterial properties	https://doi.org/10.1038/s41598-020-71610-w	biomaterial extracted from lime peel on FTO substrate.	XRD, SEM ,AFM, Raman,Spin coating.	From spun coated techniques bioactive LPE thin dilms were synthesized on a FTO substrate. It also investigated that this films shows significant antibacterial activity against <i>E. coli</i> , <i>Klebsiella pneumonia</i> , <i>Bacillus subtilis</i> , and active <i>Staphylococcus aureus</i>

The link of the information of thin film having antibacterial activity is given in the table with detailed information is provided below :-

<https://in.docworkspace.com/d/sIK7RvLI98MqjggY>

Conclusions:-

The detailed literature studies on Antibacterial activity used of metal oxide thin films has scope in this field of application.

Future Prospects :-

Tungsten oxide, the stable inorganic metal oxide has metal in variable oxidation state and hence in near future, the suitable method for synthesis will be selected and deposited films will be applied for antibacterial. In this case, the method of deposition, preparative parameters and characterization plays very vital role.

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