



"NANO-COATING OF HYDROPHOBIC, ANTI-BACTERIAL ZNO, TIO₂ NANOMATERIALS ON TEXTILE"

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ABSTRACT:

In the recent years Nanotechnology research has providing innovative solutions in the field of Biomedical, Material science, Optics, and Electronics. Nanoparticles are the nucleus of Nanotechnology. They play a plentiful role in various fields. As their size reduces, they show unique Mechanical, Physical, Chemical, Biological, Optical, Electronic properties, etc. As we know the ancient empires of the world are remembered for their large-scale feats like Machu Picchu in Peru, the Pyramids in Egypt, and Parthenon in Greece. The craftsmen of those eras were also skilled at engineering at the opposite end of the spectrum at the nanoscale. The manipulation of material at the atomic and molecular scale to create new functions and the properties sounds like, it should be an intensely modern concept. But artisans from the past also controlled matter at the tiniest scale as they were working in a branch of nanotechnology on nanocomposites. Nanocomposites are the bulk materials in which nanoparticles are mixed to improve the properties of the overall or composite material. There are several relatively famous examples of ancient artefacts created using nanocomposites.



KEYWORDS: Nanotechnology research, Electronic properties, solvothermal synthesis, physical and chemical methods.

INTRODUCTION



Figure no. 1:- Lycurgus cup

The Lycurgus cup is a stunning decorative Roman treasure from about AD400, it is made up of glass that changes color when light is shone through it. The glass contains a gold- silver alloyed design using nanoparticles, which are distributed in such a way to make the glass look green in reflected light but when light passes through the cup, it reveals a brilliant red. Another corrosion-resistant azure pigment known as Maya Blue, which is first produced in AD800, was discovered in the pre-Columbian Mayan city of Chechen Itza. It is a complex material containing clay with nanopores into which indigo dye was combined chemically to create an environmentally stable pigment. Damascus steel swords from the Middle East were made between AD300 and AD1700 and known for their impressive strength, shatter resistance, and exceptionally sharp cutting edge. The steel blends contain oriented nanoscale wire and tube-like structures, which certainly enhanced the material's properties.

Historical Perspectives

Nanoscience was a part of our heritage well before the awareness about the actual concept of nanoscience and nanotechnology. Since thousands of years' nanotechnology has been used in various applications. The ancient arts became a historical place to visit. Those people do not know the principle behind this but they knew the application. Firstly the professor of Californian institute Richard Phillips Feynman delivered a lecture in American Physical Society, in that session he mentioned about the technology as **"There's Plenty of Room at the Bottom"** on December 29, 1959. This means that there is a lot of space goes down to the smaller and smaller. The term 'Nanotechnology' was firstly introduced by the Japanese scientist Norio Taniguchi at the international conference on industrial production in Tokyo in 1974 to describe the super-thin processing of materials with nanometer range accuracy and the creation of nano-sized mechanism.

Concept of Atomism

The roots of atomism are recorded in India 2600 years ago. Hindu sage Kannada has first proposed the atomistic theory. From Buddha biography *Lalitvistara* 2200 years ago, the size of an atom was estimated to be 10^{-10} m. In the fifth and fourth centuries, B.C. *Leucippus* a Greek philosopher invented the concept of atomism (from the Greek *Atomos*, which means uncut). He stated that matter is consists of invisible particles. In 1805 John Dalton was reconfirmed that elements are made of atoms. Natural fibers have been used by humans since ancient times for body protection. Food, Clothes, and Shelter is the primary need of human beings. Our ancestors used fur and animal skin for dressing and protection from the environment such as sunlight burning, but very soon they started to use vegetal fibers to make rudimentary fabrics. There is evidence of the use of dyes on fibers and cloths are more than 30,000 years ago. Those are of vegetal fibers such as Cotton. Animal fibers such as Silk, Wool, etc. to produce yarns then weave them in a systematic and overlapping manner to form textiles by handmade process. Further evolution changed by developing industries to manufacture textiles using machines that speeded up the manufacturing of fabrics and made them more affordable. In the twentieth century, there was a technological revolution with the synthesis of artificial fibers such as Rayon, Nylon, or Polyester with good quality and low-cost production techniques that rapidly gave those fibers a significant market. Due to growing market demand, the researchers have focused their attention on the development of multifunctional textiles such as UV protection, Self-cleaning, Lotus effect of Super-hydrophobicity, Fire retardancy, Moisture management, Antibacterial, Antifungal, Wound dressing Fabrics using Nanoparticles. An excellent UV protection property is shown by TiO₂ and ZnO nanoparticles. They give protection by reflecting, scattering, or absorbing harmful UV radiation which comes from the Sun. Antimicrobial and Antifungal materials are Nano-sized Ag, Au, TiO₂, and ZnO nanoparticles.

Hydrophobicity:-

In chemistry, hydrophobicity is the physical property of a molecule (known as a hydrophobe) that is seemingly repelled from a mass of water. (Strictly speaking, there is no repulsive force involved; it is an absence of attraction.) In contrast, hydrophiles are attracted to water. Hydrophobic molecules

tend to be nonpolar and, thus, prefer other neutral molecules and nonpolar solvents. Because water molecules are polar, hydrophobe does not dissolve well among them. Hydrophobic molecules in water often cluster together, forming micelles. Water on hydrophobic surfaces will exhibit a high contact angle.

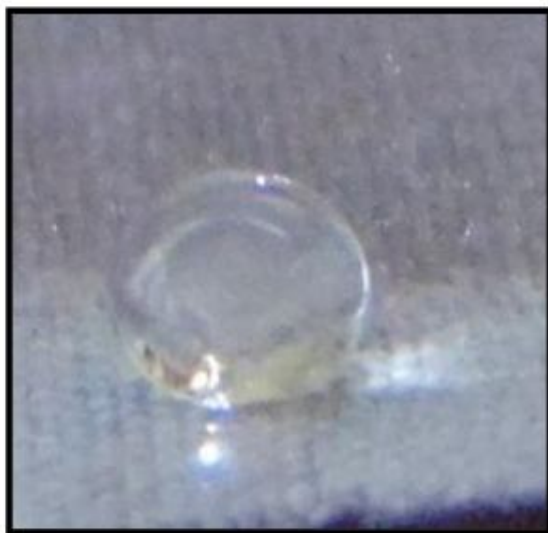


Figure no. 2:- Hydrophobic fabric

Contact Angle:-

The contact angle is an angle that is conventionally measured through the liquid drop on the substrate, where a liquid comes in contact with a solid surface as a substrate. In 1805, Thomas Young defined the contact angle θ by analysing the forces acting on a fluid droplet resting on a solid surface surrounded by a gas.

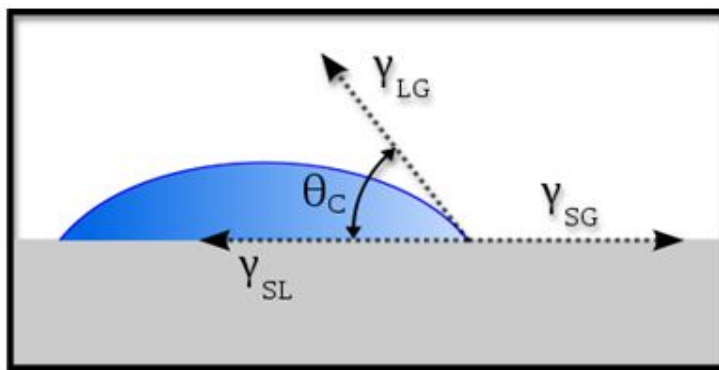


Figure no. 3:- Contact Angle

A liquid droplet rests on a solid surface and is surrounded by gas. The contact angle, θ is the angle formed by a liquid at the three-phase boundary where the liquid, gas, and solid intersect.

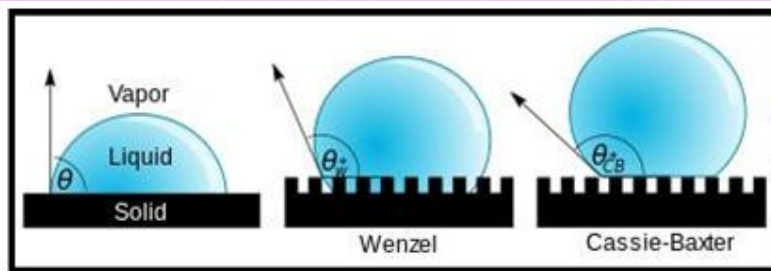


Figure no. 4:- Contact angle of hydrophilic, hydrophobic, superhydrophobic.

A droplet resting on a solid surface and surrounded by a gas forms a characteristic contact angle θ . It quantifies the wettability of a solid surface by a liquid via the Young equation. A system or a matter of solid, liquid and vapor at a given temperature and pressure has a unique contact angle. Based on interfacial energies, the surface of the droplet or a liquid bridge between two surfaces can be described by the Young-Laplace equation. This equation is applicable for three-dimensional axisymmetric conditions and which is highly non-linear. This is due to the mean curvature term which includes products of first-order and second-order derivatives of the drop shape function $f(x, y)$:-

$$\kappa_m = \frac{1}{2} \frac{(1 + f_x^2)f_{yy} - 2f_x f_y f_{xy} + (1 + f_y^2)f_{xx}}{(1 + f_x^2 + f_y^2)^{3/2}}.$$

Figure no. 5:- Formula of Contact Angle

Solving this elliptic partial differential equation that governs the shape of a three- dimensional drop, in conjunction with appropriate boundary conditions, is complicated, and an alternate energy minimization approach to this is generally adopted. The shapes of three- dimensional sessile and pendant drops have been successfully predicted using this energy minimization method.

Aims and Objectives

Aims-

- To prepare UV protective, Hydrophobic, Flame retardant Textile by coating ZnO and TiO₂ nanoparticles on it to make it an unique or multifunctional fabric.

Objectives-

- To synthesize ZnO and TiO₂ by Sol-Gel Method.
- Characterization of synthesized nanoparticles by UV-Vis Spectroscopy, Fourier Transform Infrared Spectroscopy and X-ray Diffractometer.

Methods

Coating of ZnO and TiO₂ on cotton fabric:-

➤ Ultrasonic probe sonication:-

- Initially plain white cotton fabric has been washed using a mild soap then twice rinsed using acetone and 75% ethanol.

ZnO is an amphoteric oxide and which is insoluble in water. Priorly ZnO powder can be dispersed to make a proper solution, using Deionised water and kept the fabric inside it and sonication has been carried out for 20mins Similarly TiO₂ is also coated using the same procedure.



Figure no. 6:- Ultrasonic Probe Sonicator



Figure no. 7:- Beaker contains dispersed ZnO, TiO₂ nanoparticles solution and plain white cotton fabric for coating

- Initial and final weight of fabric has been noted. Initial weight – 1.268gm
Final weight – 1.586gm
- Principle behind this method is, prepared ZnO and TiO₂ nanoparticles strongly collide on the fabric due to Ultrasonic waves and get adhered on its surface.
- This method is also called as Stone Throw Method, forcefully nanoparticles get to throw down, due to throwing they go and get rest in the gap of fabric pores.

Results and Discussion:-

Characterization of ZnO:-

➤ Characterization of ZnO by UV-Vis Spectroscopy:-

UV-Vis spectroscopy is used to determine the excitation wavelengths and the absorbance spectra by a particular sample. The π -electrons or nonbonding electrons (n-electrons) of molecules can absorb the energy of ultraviolet or visible light depending upon the energy gap up to higher anti-bonding molecular orbitals to excite themselves. The UV-Vis spectrum of ZnO nanoparticles with Barium Sulphate (BaSO₄) characterized by a strong absorption was collected in the range of 200-

800nm at room temperature. The absorbance peak at 374nm, which shows the characteristic absorption peak for wurtzite hexagonal pure ZnO.

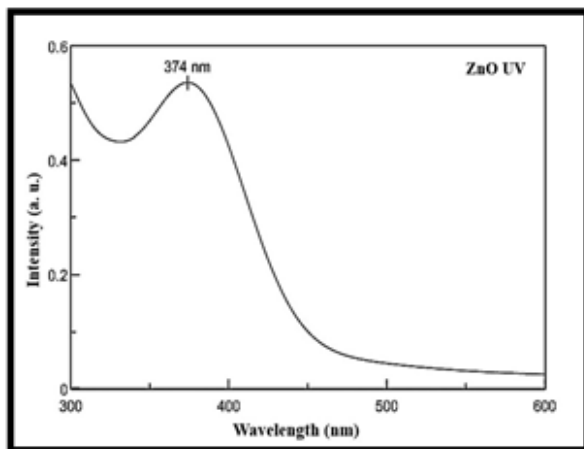


Figure no. 8:- Characterization of ZnO by UV-Vis Spectroscopy

➤ **Characterization of ZnO by Fourier Transform Infra-red Spectroscopy:-**

Fourier Transform Infra-red Spectroscopy is an analytical technique used to identify organic, polymeric and in some cases inorganic materials. In this analysis infrared light is used to scan the test samples and observe chemical properties. It shows the bonds between different elements absorb the light at different frequencies that can be measured using an infrared spectrometer which produces the output of an infrared spectrum. It can detect the functional groups and characterize covalent bonds. ZnO nanoparticles were further characterized using **PERKIN ELMER, USA (L160000R)** instrument in the disperse reflectance mode at a resolution of 4 cm⁻¹ blended in KBr pellets, and the Spectra were collected in the wavelength range of 500-4000 cm⁻¹.

Wave number (cm ⁻¹)	Functional group
1000-1250	C-O stretching
1250-1750	C-H bending
2250-2500	O=C=O stretching
3000-3750	O-H stretching

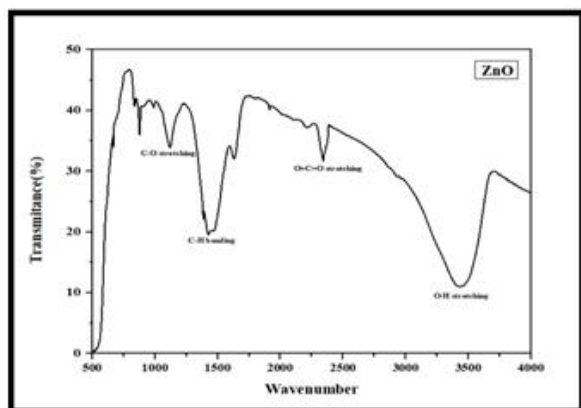


Figure no. 9:- Characterization of ZnO by FT-IR Spectroscopy

➤ X-Ray Diffraction analysis:-

In XRD, a beam of X-ray is bombarded on the sample surface, which in turn forms a diffraction pattern. The pattern contains the information of the interatomic distance of carbon atoms, revealing the state of crystallinity of the materials under study.

In this study, a sharp peak between 35-40° (2θ) angle in the XRD pattern indicated a highly crystalline show 101 indices of crystallinity.

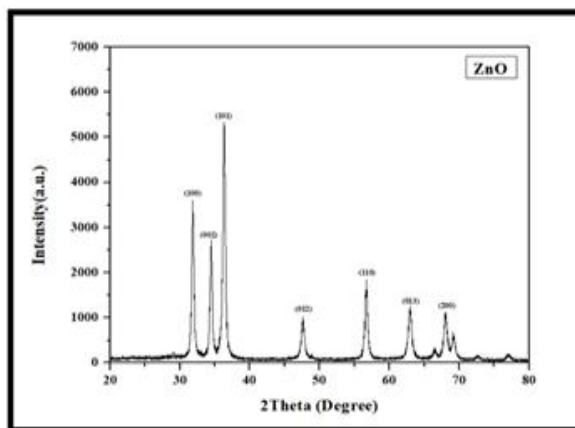


Figure no. 10:- Characterization of ZnO by X-Ray Diffraction analysis

➤ Characterization of TiO₂:-

1. Characterization of TiO₂ by UV-Vis Spectroscopy-

The observed UV absorbance of TiO₂ indicates that formed TiO₂ nanoparticles can react with deep UV and corresponds to the reaction mechanism, which tends to de-bond the atoms with the higher volent bond.

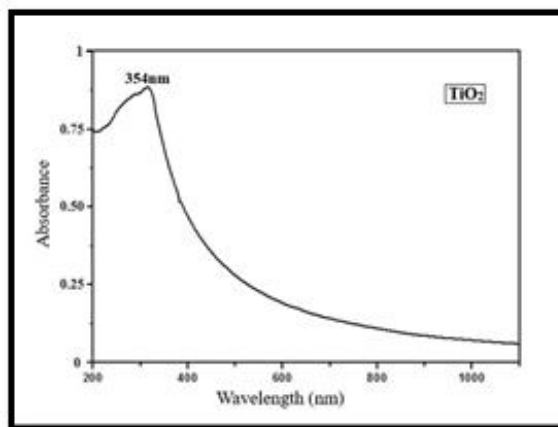


Figure no. 11:- Characterization of TiO₂ by UV-Vis Spectroscopy

2. Characterization of TiO₂ by Fourier Transform Infra-red Spectroscopy:-

TiO₂ nanoparticles were further characterized using **PERKIN ELMER, USA (L160000R)** instrument in the disperse reflectance mode at a resolution of 4 cm⁻¹ blended in KBr pellets, and the Spectra were collected in the wavelength range of 500-4000 cm⁻¹.

Wave number (cm ⁻¹)	Functional group
1386	C-H bonding
1623	C=O stretching
2800-3500	N-H stretching

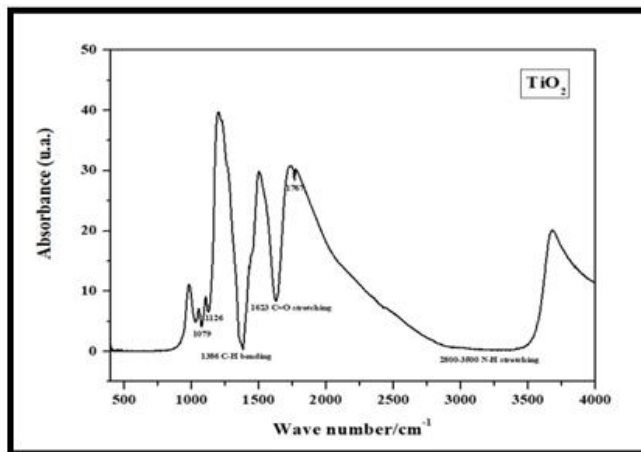


Figure no. 12:- Characterization of TiO₂ by FT-IR Spectroscopy

Hydrophobicity of ZnO:-

Before Coating	After Coating
 Water 84.18°	 Water 119.4°
 Blood 71.05°	 Blood 121.08°
 Urine 82.40°	 Urine 110.17°

Figure no. 13:- Hydrophobicity of ZnO

The contact angle of Plain White Cotton fabric before coating shows hydrophilic results that means the molecular entity of fabric is attracted to the Water, Blood, and Urine molecules and absorb them frequently, while the contact angle of ZnO coated fabric shows hydrophobic effect which does not attracted by the water, Blood, and Urine molecules and may seem to be repellent by it.



Figure no. 14:- Hydrophobicity of TiO₂

The contact angle of Plain White Cotton fabric before coating shows hydrophilic results that means the molecular entity of fabric is attracted to the Water, Blood, and Urine molecules and absorb them frequently, while the contact angle of ZnO coated fabric shows hydrophobic effect which does not attracted by the water, Blood, and Urine molecules and may seem to be repellent by it.

Anti-bacterial activity of ZnO using *Escherichia coli* and *Proteus vulgaris* :-

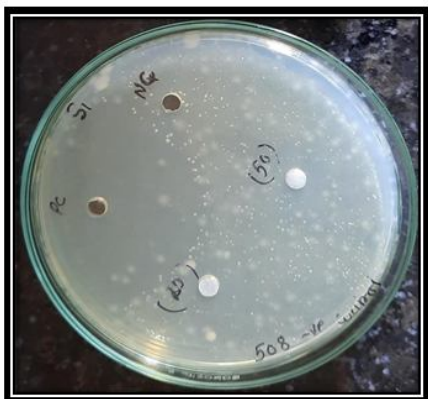


Figure no. 15:- Anti-bacterial activity of ZnO nanoparticles the shows zone of inhibition against *E. coli* Gram-negative bacteria

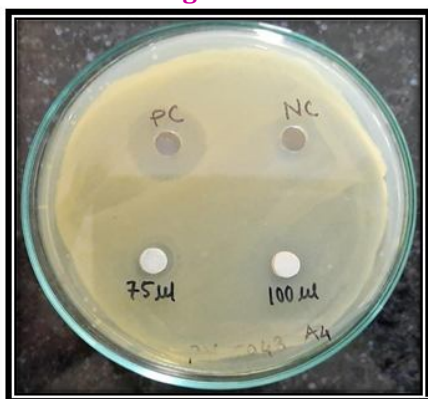


Figure no. 16:- Anti-bacterial activity of ZnO nanoparticles shows the zone of inhibition against *Proteus vulgaris* Gram-positive bacteria

Washing cycles of coated fabric:-

Obtained results indicated that treated fabric samples with ZnO and TiO₂ nanoparticles showing the same results as hydrophobic after 10 washing cycles.



Figure no. 17:- Washing cycles of coated fabric

CONCLUSION:

In the twentieth century, there was a technological revolution with the synthesis of artificial fibers such as Rayon, Nylon, or Polyester with good quality and low-cost production techniques that rapidly gave those fibers a significant market. Due to growing market demand, the researchers have focused their attention on the development of multifunctional textiles such as UV protection, Self-cleaning, Lotus effect of Super-hydrophobicity, Fire retardancy, Moisture management, Antibacterial, Antifungal, Wound dressing Fabrics using Nanoparticles. ZnO, TiO₂, CuO nanoparticles show good Flame Retardancy property. The contact angle is an angle that is conventionally measured through the liquid drop on the substrate, where a liquid comes in contact with a solid surface as a substrate. To prepare UV protective, Hydrophobic, Flame retardant Textile by coating ZnO and TiO₂ nanoparticles on it to make it an unique or multifunctional fabric. Principle behind this method is, prepared ZnO and TiO₂ nanoparticles strongly collide on the fabric due to Ultrasonic waves and get adhered on its surface.

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