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Nanonization Of Zinc Oxide By Top-Down Approach For Multiple Applications

Adarsh R. Malgave*, S. S Suryawanshi , Dr. Sachinkumar V. Patil

Ashokrao Mane College of Pharmacy, Peth-Vadgaon, Kolhapur, Maharashtra, India. (416112)

Affiliated to Shivaji University, Kolhapur, Maharashtra.

ABSTRACT:

Nanoscience and nanotechnology are the study and application of extremely small objects, and they can be applied in chemistry, biology, physics, materials science, and engineering, among other subjects. The exceptional physical and chemical properties of zinc oxide nanoparticles (ZnO) provide advantages. It is a low-cost material used in the cosmetics sector, nanofertilizers, and electrical devices, as well as a good agent for bioimaging and targeted medication and gene delivery, as well as an excellent sensor for detecting environmental toxins and remediation.

A disinfectant made from newly synthesised zinc (II) oxide nanoparticles (ZnO-NPs) has been tested. For the developing corona virus, a nano-spray has been developed (SARS-CoV-2). Various spectroscopic analysis (FT-IR, UV, and XRD) and surface analysis techniques were used to completely chemically analyse the produced (ZnO) nanomaterial. This review focuses on ZnO-NPs, which have potent antiviral activity against SARS-CoV-2 at very low concentrations and can trigger many free radicals, causing oxidative stress to SARS-CoV-2 and severe damage to SRAS-CoV-2 cellular membranes, which is a critical result in the fight against SARS-CoV-2.

Inorganic physical sun blockers such as titanium dioxide (TiO2) and zinc oxide (ZnO) are commonly used in sunscreens. The combination of TiO2 and ZnO ensures broad-band UV protection since TiO2 is more effective in UVB and ZnO is more effective in UVA. Microsized TiO2 and ZnO have been increasingly substituted with TiO2 and ZnO nanoparticles (NPs) (100 nm) to address the cosmetic issue of these opaque sunscreens. This paper examines the considerable impact on sunscreen UV attenuation when microsized TiO2 and ZnO particles are substituted with NPs, as well as the physicochemical factors that influence NP sunscreen effectiveness and safety

Key Words: Zinc oxide Nanoparticles (ZnO-NPs), Sunscreen, Coronaviruses (CoVs), Nanotechnology, Disinfectant.

INTRODUCTION

Zinc oxide has the formula ZnO and it is an inorganic substance. Rubbers, plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, meals, batteries, ferrites, fire retardants, and first-aid tapes all contain zinc oxide, which is a white powder that is insoluble in water. Although it occurs naturally as the mineral zincite, most zinc oxide is produced synthetically.

Figure No 1. Zinc Oxide Powder

Pure ZnO is a white powder, but in nature it occurs as the rare mineral zincite, which usually contains manganese and other impurities that confer a yellow to red color. Zinc oxide is an amphoteric oxide. It is nearly insoluble in water, but it will dissolve in most acids, such as hydrochloric acid. [1, 2, 3]

$ZnO + 2\ HCl \rightarrow ZnCl_2 + H_2O$

Solid zinc oxide will also dissolve in alkalis to give soluble zincates:

$ZnO + 2\ NaOH + H_2O \rightarrow Na_2[Zn(OH)4]$

Introduction to Nanotechnology

NANO & TECHNOLOGY: In the metric system, A nanometre is a unit of length equal to one billionth of a metre (10^{-9}).

Technology is the creation, application, and understanding of tools, machines, and processes to solve a problem or carry out a specified purpose.

Nanotechnology is defined as the study and use of structures between 1 nm and 100 nm in size. To put that in perspective, it would take 800 nanometer particles lined up side by side to equal the breadth of a human hair.

While this is the most widely accepted definition of nanotechnology, researchers with different areas of interest have slightly different definitions. [4]

History

Dr. Richard P. Feynman, well-known physics professor, offered the first concept in 1959.

Nanotechnology was born with the invention of the scanning tunnelling microscope in 1981 and the discovery of fullerene (C60) in 1985.

Norio Taniguchi created the phrase "nanotechnology" in 1974. [4]

History of Nanotechnology [4]

Sulfide nanocrystals were used to colour hair by the Greeks and Romans 2000 years ago.

1000 Years Ago (middle Ages) - Gold nanoparticles of various sizes were employed to create varied hues in stained glass windows.

1959 - R. Feynman is a famous physicist

1974 - "Nanotechnology" Norio Taniguchi uses the term nanotechnology for the first time

1981 - IBM develops Scanning Tunneling Microscope

1985 "Buckyball" - Scientists at Rice University and University of Sussex discover Co

1986 - "Engines of Creation" - First book on nanotechnology by K. Eric Drexler. Atomic Force Microscope invented by Binnig, Quate and Gerbe

1989 - IBM logo made with individual atoms

1991 - Carbon nanotube discovered by S. lijima

1999 - "Nanomedicine" - 1st nanomedicine book by R. Freitas

PROPERTIES

1) Nanotechnology is already making today's products
2) Lighter
3) Stronger
4) Faster
5) Smaller
6) More Durable

Approaches in nanotechnology

1. **Bottom up:**

Different materials and devices are built from their own molecular components in the bottom up approach. They construct themselves chemically by identifying molecules from their own breed. Watson-Crick base pairing and nano-lithography are examples of molecular self assembly.

2. Top down:

In top down approach nano objects and materials are created by larger entities without bouncing its atomic reactions usually top down approach is practiced less as compared to the bottom up approach. Solid-state techniques can also be used to create devices known as nano electromechanical systems or NEMS, which are related to micro eletromechanical systems or MEMS. MEMS became practical once they could be fabricated using modified semiconductor device fabrication technologies, normally used to make electronics. [4]

Materials used

Zinc oxide: Dirt repellent, hydrophobic, cosmetics & stain resistant

Silver ion: Healing property

Aluminum silicate: Scratch resistance

Gold ion: Chip fabrication, drug delivery [4]

Advantages and Disadvantages of Nanotechnology [5]

Advantages of nanotechnology	Disadvantages of nanotechnology
• Enhancement of solubility and bioavailability • Protection from toxicity • Enhancement of pharmacological activity • Enhancement of stability • Improve tissue macrophage distribution • Sustained delivery • Protection from chemical (e.g., pH). physical and biological (e.g., enzymes) degradation • Enhancement of permeability (e.g., through blood brain barrier) and retention effect • Decrease side-effects of conventional drugs • Improves therapeutic effect.	• High-cost • Difficulty in scale-up processes • Easy inhalability of nanoparticles resulting into lung diseases • High immunogenicity • Chances of poor targeting • High ability to aggregate in biological systems

Applications of ZnO:

1) For material science applications, zinc oxide has high refractive index, high thermal conductivity, binding, antibacterial and UV-protection properties.

2) It is added into materials and products including plastics, ceramics, glass, cement, rubber, lubricants, paints, ointments, adhesive, sealants, concrete manufacturing, pigments, foods, batteries, ferrites, fire retardants, etc.

3) Numerous applications involve the dispersions of zinc oxide in a suitable solvent to get the slurry for further use in the respective industry.

Objectives:

1) The raw zinc oxide is hydrophobic in nature and comes in micron size.

2) The pharmaceutical and cosmetic industry requires the nano sized dispersions of, zinc oxide for sunscreens and to be use in nappy rash cream.

3) It's application of nano dispersion of zinc oxide is as pesticide for mangoes and pomegranate plants.

4) The top down approach for reducing the size of zinc oxide to get nano sized dispersions with the help of ball mill for pharmaceutical and agrochemical industry was explored in this research project.

LITERATURE REVIEW

Literature review on zinc oxide Nanoparticles used in sunscreen

1) Osmond . M.J. et al (2010) [6]

Absorption through the skin There have been no research that we are aware of that look into the hazard potential or fate of ZnO nanoparticle dust that may settle on exposed skin from the air or direct contact with other surfaces. There are few studies that have looked into nanoparticles suspended in emulsions or sunscreen formulations , however these will be discussed in the section on product use.

2) Popov et al. (2005) [7]

Making sunscreens more aesthetically pleasant by making them seem transparent on the skin. Nanosized metal oxide particles, in addition to easing consumer acceptance, may also provide better UV protection than their microsized counterparts, at least in the UV B zone.

3) Wolf et al. (2001) [8]

These particles reflect and scatter light in the standard pigment size ranges (150–300 nm for TiO2 and 200–400 nm for ZnO), making the sunscreens seem white. However, as particle sizes shrink to sub-micron (nano) dimensions (usually between 20 and 150 nm for TiO2 and 40–100 nm for ZnO), UV radiation is absorbed and scattered, and visible wavelengths are largely absorbed.

4) Mitchnick et al. (1999); Pinnell et al.(2000) [9,10]

As an active physical constituent in sunscreens, zinc oxide has remarkable characteristics. It absorbs UV more effectively than TiO2 over a wider range of wavelengths, especially in the UVA area, and is hence utilised as the only active ingredient in some broad-spectrum sunscreens. The utilisation of ZnO nanoparticles slated for use in current sunscreens is the subject of this review.

5) Pinnell et al.(2000) [10]

When assessing the potential dangers connected with their use, keep in mind that ZnO nanoparticles provide the broadest UV protection of all the active components now available in commercial sunscreens. Their use in sunscreens provides comprehensive protection against UVA and UVB's recognised carcinogenic, immunosuppressive, and photo-aging effects.

6) Cayrol et al.(1999) [11]

Metal oxide particles with intrinsic UV absorption capabilities, such as zinc oxide (ZnO) and titanium dioxide (TiO2), are commonly used as active 'physical' components. Physical UV blockers in sunscreens have been demonstrated to be quite effective in shielding cells from UV-induced DNA damage.

Literarure review on zinc oxide Nanoparticles used in Covid -19 [19]

1) Hamza, R.Z. et al (2021) [12]

Coronaviruses (CoVs) are RNA viruses that are classified as such. CoVs infect mammals and birds' upper respiratory tracts first. In humans, cough and fever are the most common signs of CoV infection, and SARS-CoV-2 can also cause breathing difficulties. Severe respiratory illnesses induced by SARS-CoV-2 are among COVID-190's clinical manifestations, such as excessive inflammation and oxidation. SARS-

CoV-2 is spreading widely in humans, and COVID-19 differs from other varieties of COVID virus (CoVs) in its effects. COVID-19 is considered a pandemic, with millions of patients infected in a single year all over the world. Emerging diseases caused by corona viruses have been a major source of concern around the world.

2) Zhou, P. et al. (2020) [13]

Zinc has antiviral properties and may improve lymphocyte response to gene transcription or bio-molar function. Zinc oxide has a large band gap and belongs to the II-IV semi-conductor group, with binding energies of 3.2 eV and 60 meV, respectively. Zinc oxide nanoparticles have antibacterial, anti-cancer, and wound-healing characteristics, as well as the ability to block UV radiation.

3) Tsuneo, I. et al (2019) [14]

SARS-CoV-2 viruses are currently spherical in form, with a diameter ranging from 70 to 140 nanometers. Spikes cover the surfaces of SARS-CoV-2.SARS-CoV-2 is spread by infected people through exhalation or aerosol particles, which stick to surfaces and are then contacted by the receiver. Zinc is one of the most prevalent trace metals in the human body, with about 2–3 g in bone and muscle, 90 percent in other organs, and 10% in other tissues. Zinc is extremely important in the cells. Zn has a modest cytotoxicity and affects a number of cellular death regulators.

4) Ghaffari et al. (2019) [15]

Discovered that Zn^{2+} ions prevented viral reproduction and increased the intracellular Zn2+ content, which can effectively impede the replication of a range of RNA viruses. The goal of this study is to assess the antiviral activity of synthesised ZnO-NPs against SARS-CoV-2 infection using chemical characterization of ZNO nanoparticles, as well as to assess its use as a nano-spray against SARS-CoV-2 infection, as well as to estimate cytotoxicity and suggest future studies to improve the antiviral activity of ZnO-NPs.

5) Farouk, F. et al (2018) [16]

The process by which an infection develops to viral disorders, including viral entrance and shedding of diseases like COVID-19, is known as viral pathogenesis.

6) Tavakoli, A. et al (2018) [17]

Zinc's antiviral characteristics may make it useful in the fight against SARSCoV-2. Zinc supplementation has been recommended as a way to improve the efficacy of other medications now being studied, such as hydroxychloroquine. ZnO-NPs lowered virus titer and suppressed virus replication by 92 %.

7) Sunada, K .et al (2012) [18]

Zn has antiviral properties and could be used to treat a variety of respiratory viruses, including SARS-CoV-2. As a result, incorporating vitamins and minerals in one's diet can be utilized in conjunction with antiviral medications to treat COVID-19 disease.

MATERIALS & METHODS:

Materials:

Zinc oxide powder (size ≈ 0.6–1 μm, purity 99.9%, Loba, Chemi, Pvt. Ltd, India), Light Shea Butter, Cyclomethicone, Dimethicone Copolyol, Silicone elastomer gel, Cyclopentasiloxane, SS Beads (diameter 15 mm, weight 32 gm) etc.

Methodology:

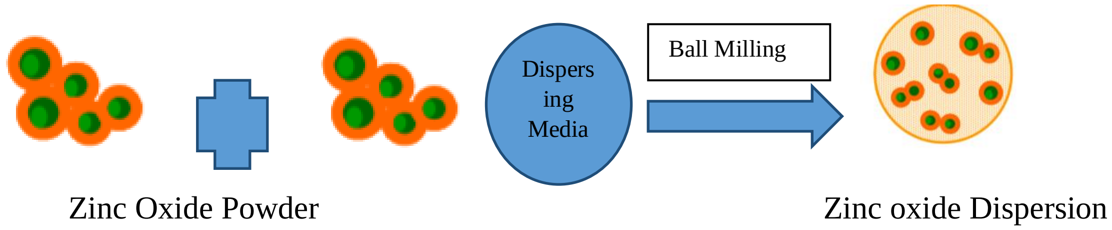


Figure No 2 : Nanoparticles of zno dispersion by using Ball mill

The mechanical milling was performed in a horizontal oscillatory mill (Remi Lab Mumbai). The mixture ratio of steel balls and ZnO powders was around 15:1 by weight percent. The milled materials were used directly with no added milling media. Five balls were kept in each cell along with 10 g of the sample powder. Two parallel cells were used in this experiment (the total weight for the sample powder was 20 g) [1-3]

Formula:

Batch No	Dispersion Media	Milling Time	Particle Size in nm
Zn Dis 01	Cyclopentasiloxane	24 Hours ± 30 Min	178 ± 10
Zn Dis 03	Cyclopentasiloxane	26 Hours ± 30 Min	124 ± 8
Zn Dis 03	Cyclopentasiloxane	28 Hours ± 30 Min	116 ± 8
Zn Dis 04	Dimethicone Copolyol	26 Hours ± 30 Min	154 ± 5
Zn Dis 05	Cyclomethicone	26 Hours ± 30 Min	179 ± 10

ZINC OXIDE NANOPARTICLES IN SUNSCREEN

Nanoparticles are one-twentieth the thickness of a human hair.

Nanoparticles are smaller than 100 nanometres and invisible to the human eye - a nanometre is 0.000001 millimetre.

Microfine particles are smaller than those used in conventional white zinc sunscreens, however are larger than nanoparticles - usually in the range of 100 to 2500 nanometres.[4]

WHAT ARE SUN RAYS

The sun emits several kinds of electromagnetic radiation: Visible (Vis), Infrared (IR) and Ultra Violet (UV).

Each kind is distinguished by a characteristic wavelength, frequency and energy

Higher energy radiation can damage our skin [4]

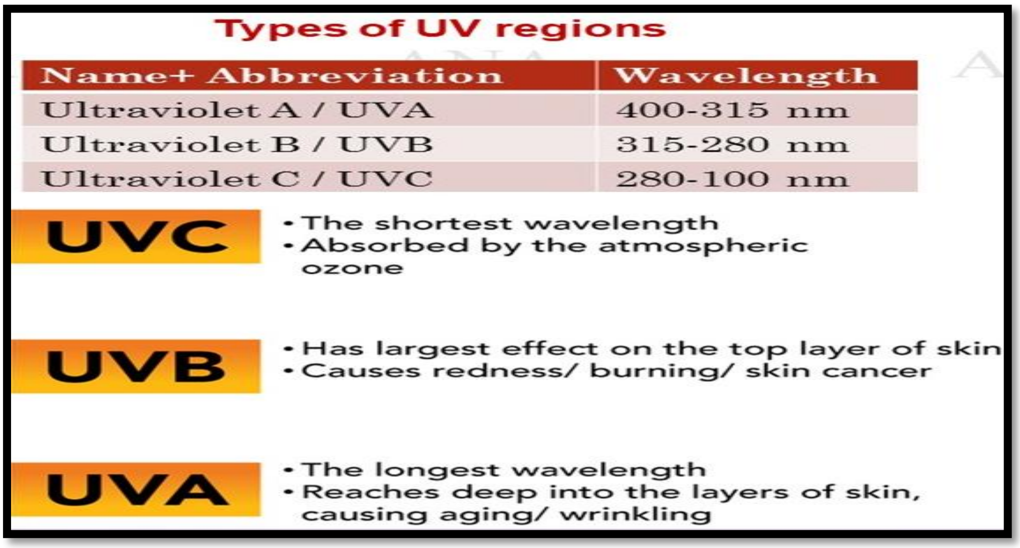


Figure No 3. Types of Sunrays

USE OF SUN-SCREEN

Too much unprotected sun exposure leads to:

Premature skin aging (e.g. wrinkles)

Sunburns

Skin cancer

NANOMATERIALS IN SUNSCREEN

sunscreens made with zinc oxide and titanium dioxide generally score well because they provide strong sun protection with few health concerns, They don't break down in the sun.

NANOMATERIALS

Titanium dioxide (TiO_2) and zinc oxide (ZnO) pigments are commonly used in personal care products to provide protection against UVA and UVB.

They attenuate UV light by absorption and scattering.

They are usually surface coated to minimize photo-catalytic activity.

They are typically produced as finer crystals from the same feed stocks and with similar processes as pigmentary grades.

zine oxide offers good protection from UVA rays-titanium oxide less so, but better than most other active ingredients.

As the field of nanotechnology develops, nanoparticles appear more frequently in consumer products. In sunscreen, zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles are used to scatter ultraviolet light. The advantage of these over larger particles is that sunscreen containing nanoparticles is transparent when applied. However, the potential health risks of exposure to nanoparticles are largely unknown.

Figure No 4 :Comparison of ZnO nanosized and large particles

Applications of zinc oxide Nanoparticles used in Covid 19

Nanoparticles have significant therapeutic potential since they are effective at low concentrations and may have powerful antiviral action against drug-resistant viruses. Nanoparticles have other essential properties, such as their adaptability for various coating types.

According to SI (IC50/CC50 1), ZnO-NPs had anti-SARS-CoV-2 action with low cytotoxicity in the current investigation. These findings are in line with those of [21] ,who discovered that when ZnO-NPs are combined with PE-Glyated-NPs, they had higher antiviral activity but lower cytotoxicity than ZNo-NPs alone and This provides a new direction for the current investigation, which is to propose ZNO-NPs as a low-cytotoxicity disinfectant against SARS-CoV-2. We recommend employing ZnO-NPs coated with PEGlyated (Polyethylene Glyated), which enhances and elevates antiviral activity against the SARS-CoV-2 virus and may lower ZnO-NPs' cytotoxicity to host cells.

More evidence for our findings and our recommendation for coating ZnO-NPs may be found in a previous work by Ghaffari et al. [15], who discovered that ZnO-NPs have stronger cytotoxicity on breast cells than PEGyated Zno-NPs. ZnO-NPs create Zn2+ ions as well as several forms of reactive oxygen, according to our theory (ROS) and These free radicals can harm proteins, lipids, carbohydrates, and DNA, leading to cell death [16]. As a result, we believe that covering ZnO-NPs with polyethylene glycol can result in significant anti-COVID-19 action, reducing cytotoxicity and preventing reactive oxygen release by masking ZNO–NPs.

Metal nanoparticles like ZnO-NPs have recently been proven to be effective against a variety of diseases, including viruses [15]. ZnO-NPs have been shown to exhibit antimicrobial properties against a variety of human diseases [22]. The majority of investigations on ZnO-NPs, however, have focused on their inhibitory effects on bacterial infections. There are also few investigations on the interaction of ZnO-NPs with viruses. In a recent study, our lab discovered that ZnO-NPs have potent inhibitory effects on SARS-CoV-2, one of the most dangerous viruses affecting human health.

ZnO-NPs are thought to have antiviral activity due to their capacity to neutralise viruses [22]. Another reason for ZnO-NPs' antiviral activity is that they may stimulate and improve the immune system's defences against viruses, resulting in significant therapeutic benefits [23]. This strategy is critical in the fight against COVID-19.

The findings of this work confirm those of [24], who revealed that a negatively charged ZnO-NP can simply trap the herpes virus and prevent it from attaching to host cells.

In contrast to the current findings, Sunada et al. [18] discovered that culturing ZnO with viruses increased cellular survival by more than 50%, whereas cellular survival decreased in the current findings, which opens the door for more research into different concentrations of ZnO-NPs to find an effective ratio against SARS-CoV-2 with low cytotoxicity.

Such data, which confirms the anti-COVID-19 activity of ZnO-NPs at very low cytotoxicity and at very low concentration (526 ng/mL), is somewhat surprising, with somewhat low cytotoxicity that can be alleviated by coating ZNO-NPs with polymeric compounds such as PEGlyated, which may decrease the particles' diameter and We believe these findings are promising in the fight against the COVID-19 pandemic because they limit the triggering adverse effects of ROS on cellular components while attaining high infective action against SARS-CoV-2 at a very low concentration.

Anti-Viral Activity and Cytotoxicity of Zinc Oxide Nanoparticles and Inhibition Activity against SARS-CoV2 [19]

ZnO-NPs showed potent antiviral activity against SARS-CoV-2 in very low concentration of 526 ng/mL. The MTT assay was used to evaluate potential cell cytotoxicity of ZnO-NPs. The results showed that 292.2 ng/mL of ZnO-NPs significantly reduced the viability of VERO-E6 cells (Figure 9) and Images of Vero-6 cell after incubation with SARS-CoV-2 (after infection) which showed potent anti-viral activity of ZnO-NPs against SARS–Cov-2, the sheet of cells treated with ZnO-NPs showing enlarged patches around SRAS-CoV-2 cells as shown in (Figure)

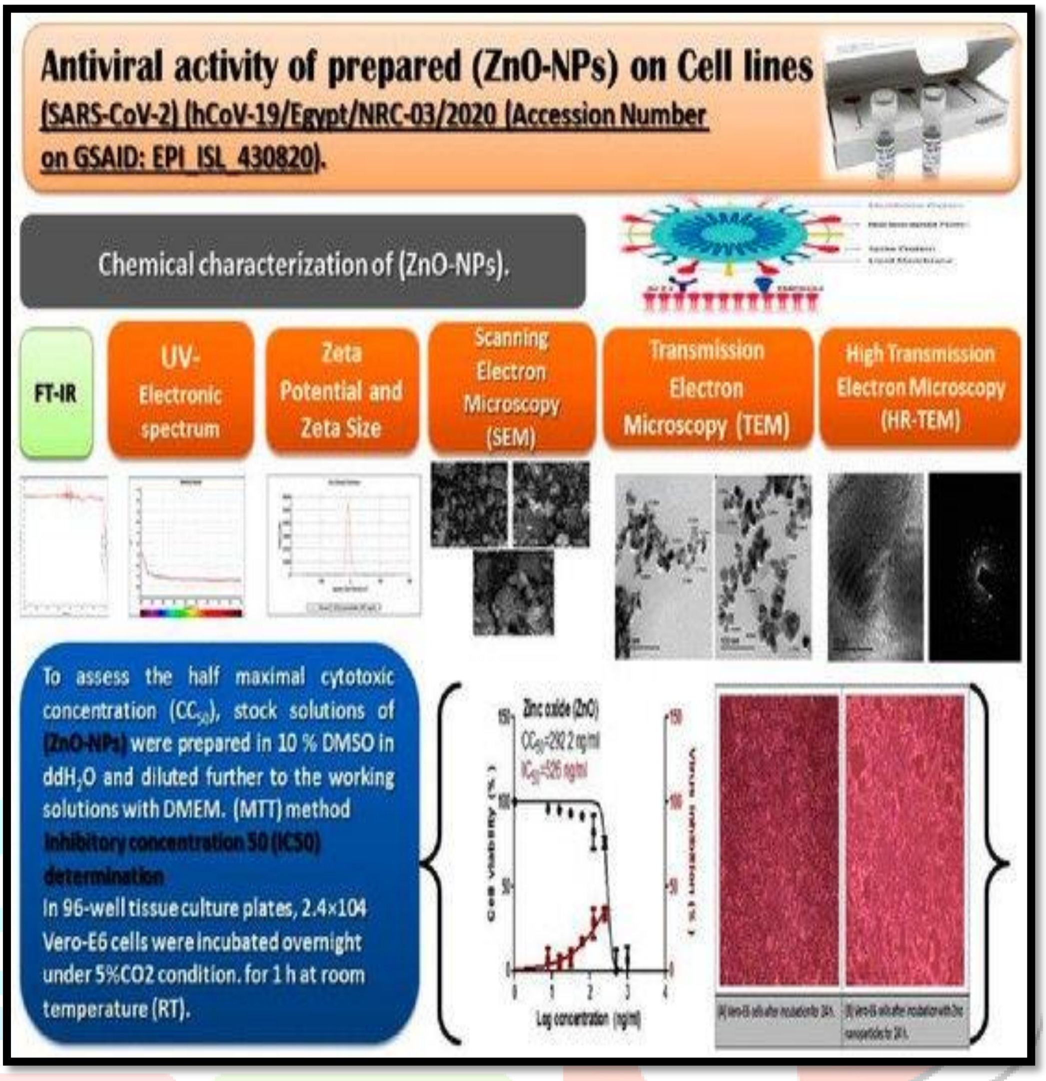


Figure No 5. Graphical abstract for the experimental work.

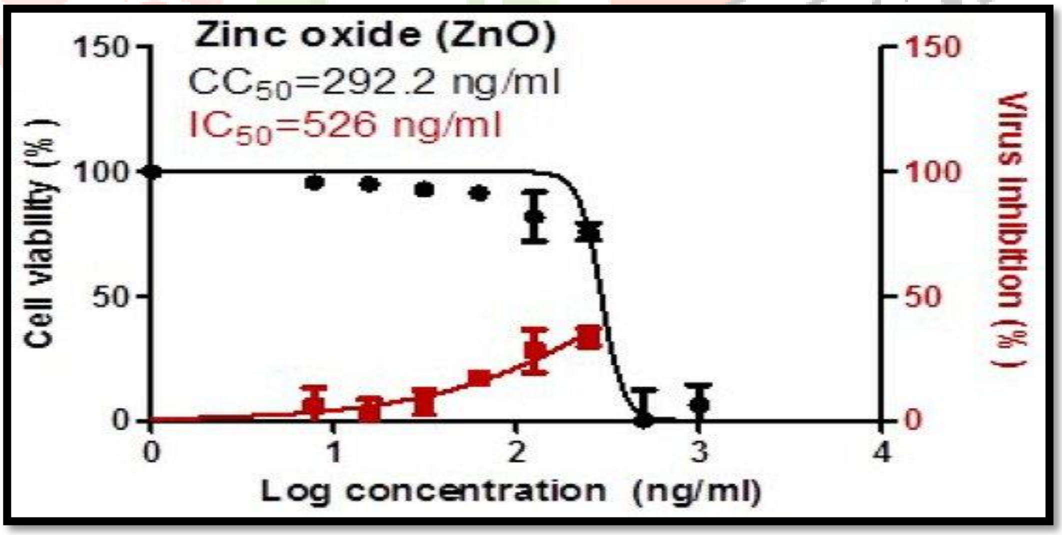
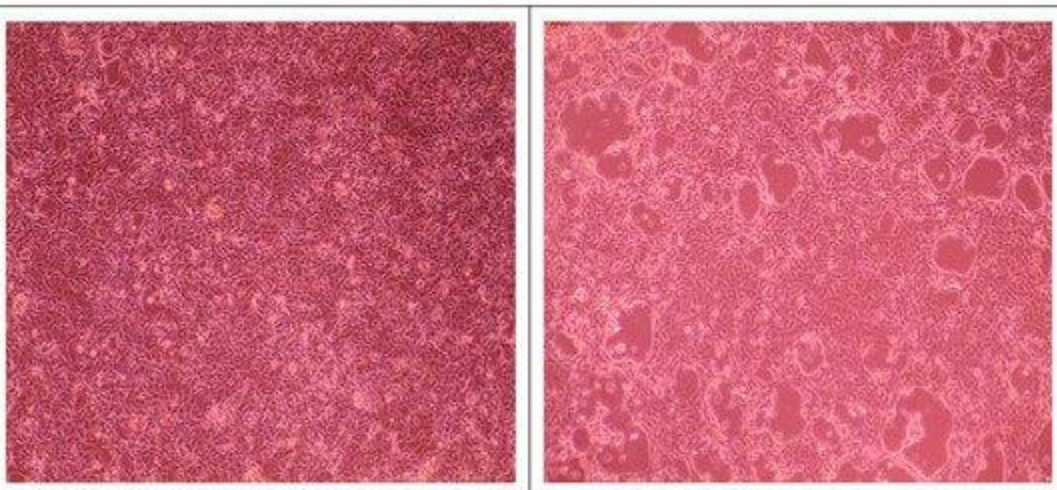
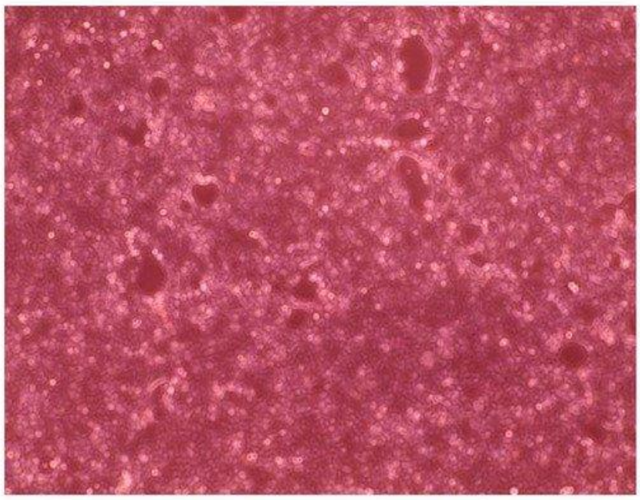


Figure No 10. Cytotoxicity and inhibitory concentration of Zno-NPs against SARS-CoV-2



(A) Vero-E6 cells after incubation for 24 h.

(B) Vero-E6 cells after incubation with Zno nanoparticles for 24 h.



(C) (SARS-CoV-2) (hCoV-19/Egypt/NRC-03/2020) incubated with Vero-E6 cell monolayers at 37 °C for 4 h after infection.

Figure No 6. Images of Vero-6 cell after incubation with SARS-CoV-2 (after infection) which showed potent anti-viral activity of ZnO-NPs against SARS–Cov-2, the sheet of cells treated with ZnO-NPs showing enlarged patches around SRAS-CoV-2 cells, thus demonstrating the ability of ZnO-NPs to disinfect SARS-CoV-2 and offer a high level of inhibition to its growth.

Evaluation of zno nps:

Physical Properties of the dispersions:

Sr. No	Parameters	Result
1	Appearance and color	White colored dispersion slurry
2	Viscosity (by Brookfield Viscometer)	7500- 12000 mPa.S
3	Assay of Zinc oxide (by Gravimetric Titration)	More than 98%

Microscopic Studies:

The developed dispersions were studied for agglomerates and also for consistency of the slurry by using electronic microscope and images were captured.

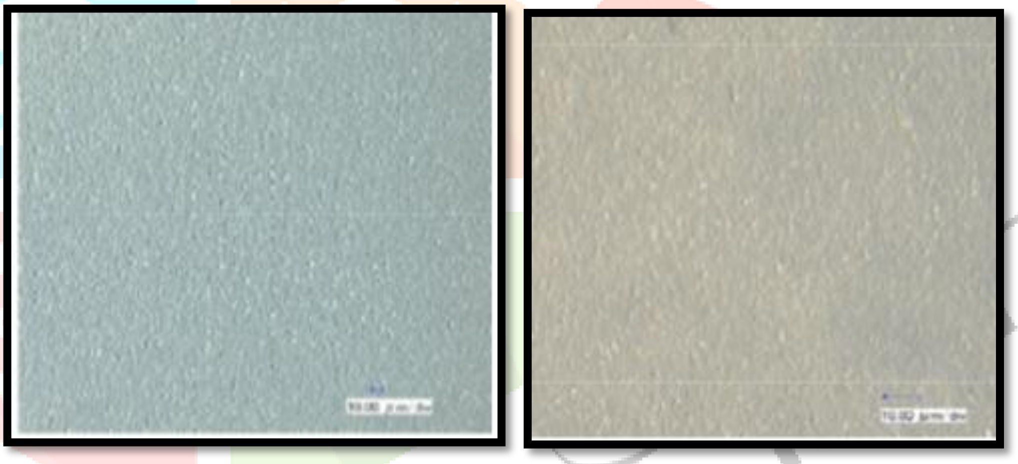


Figure No 7. Microscopic pictures of ZnO Dispersions under X 450 and X 1500 scan

2. Water & Oil Proofness Study:

Method: Applied dispersion on PET film by applicator (0.1mm). After drying, put droplet of water (blue) and squalane (red).

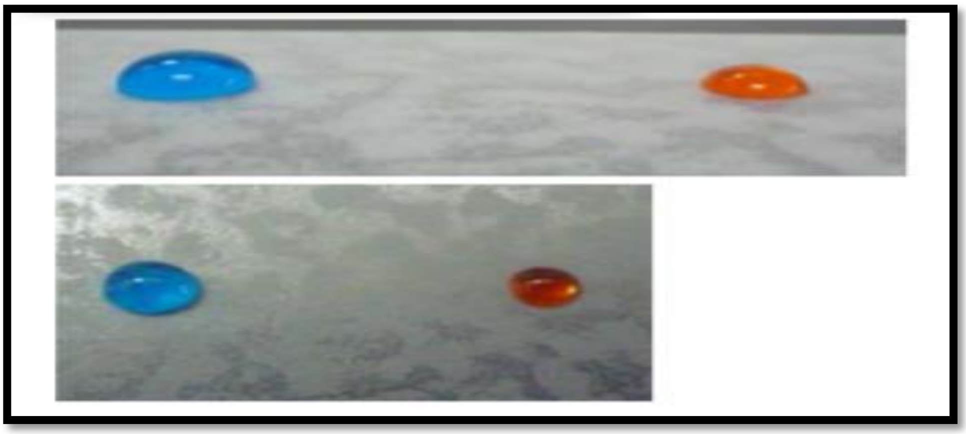


Figure No 8. ZnO Dispersion- Water and Oil Proofness Study

3. Whitish Color Change:

a) No Whitish Color Change (In Vitro) Method:

Applied Sun Screen on PET film by applicator (0.1mm). After drying, put into water for 3 minutes. Take out the film and checked the appearance.

Sunscreen with Conventional ZnO Slurry Sunscreen with silicone ZnO Slurry

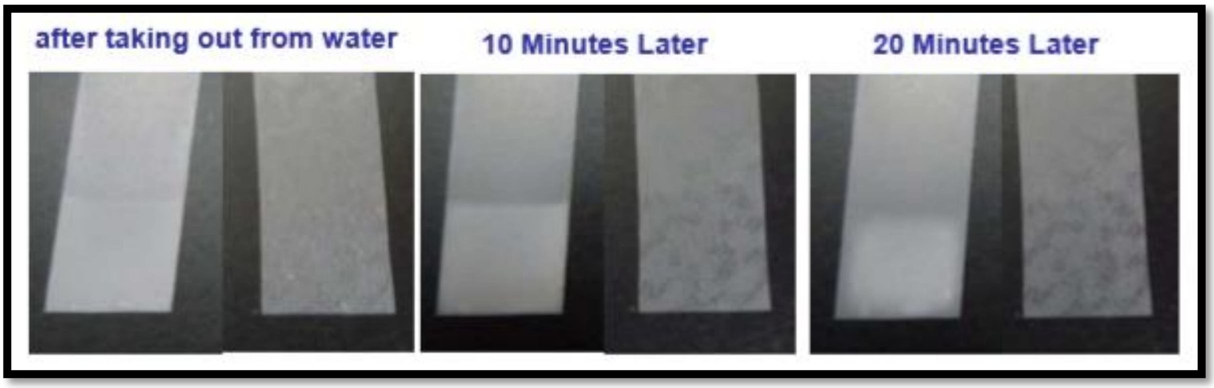


Figure No 9. Comparison of Zno Slurry on PET film

b) No Whitish Color Change (In Vivo) Method:

Applied Sun Screen gel on human skin (0.04g/20cm2), dried for 30 minutes, and put in water for 3 minutes. Took out the arm and check the appearance.

a) Sunscreen with Conventional Zinc Oxide Slurry

b) Sunscreen with silicone Zinc Oxide Slurry

Figure No 10. Comparison Zno Applied on Human Skin

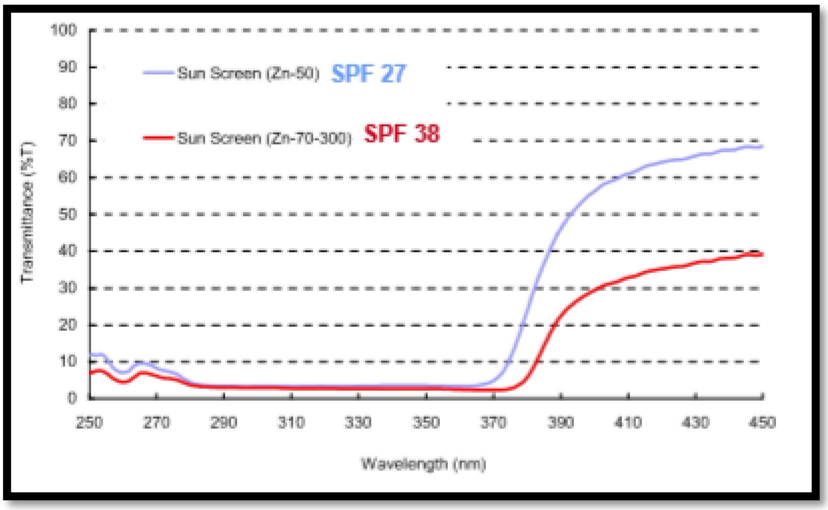


Figure No 11: SPF Determination by UV Method

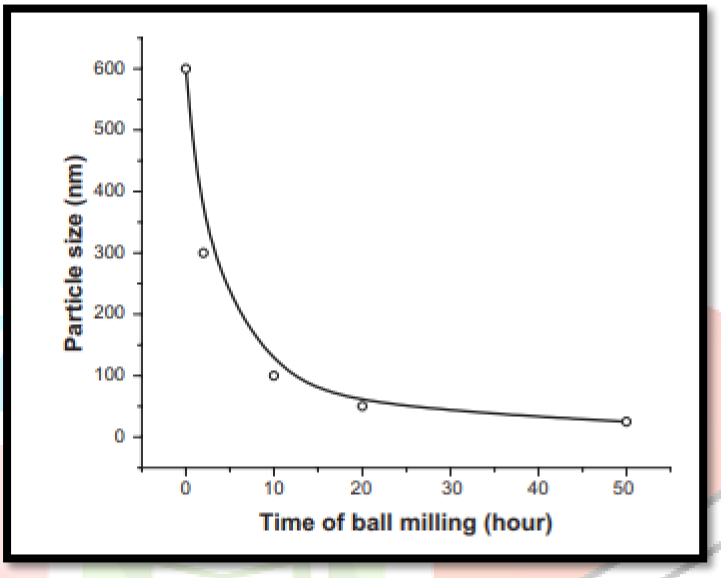


Figure No 12. Effect of milling time on Reduction of Particle size of ZnO

CONCLUSION :

These particles reflect and scatter light in the standard pigment size ranges (150–300 nm for TiO2 and 200–400 nm for ZnO), making the sunscreens seem white. However, as particle sizes shrink to sub-micron (nano) dimensions (usually between 20 and 150 nm for TiO2 and 40–100 nm for ZnO), UV radiation is absorbed and scattered, and visible wavelengths are largely absorbed. Making sunscreens more aesthetically pleasant by making them seem transparent on the skin. Nanosized metal oxide particles, in addition to facilitating consumer acceptance, may also provide better UV protection than their microsized counterparts, at least in the UVB region.

On the basis of available evidence, it is concluded that the use of ZnO nanoparticles with the characteristics listed below as a UV-filter in sunscreens at a concentration of up to 25% does not pose a risk of adverse effects in people after dermal application.

ZnO-NPs have antiviral activity against SARS-CoV-2 at very low concentrations (IC50 = 526 ng/mL) and can produce oxidative stress and severe damage to SARS-CoV-2 cellular membranes, which is an important result in the fight against SARS-CoV-2. However, we discovered that ZnO-NPs are cytotoxic to VERO-E6 cells (CC50 = 292.2ng/mL), and we urge that further prospective research be conducted using ZnO-NPs immobilisation with natural active chemicals to reduce cytotoxicity and increase antiviral efficacy against SARS-CoV-2.

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