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# Structural, Optical and Ros Generation Properties of Titanium Dioxide Nanoparticles and Its Nanocomposites with Zinc Oxide

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## Abstract

Metallic oxide nanoparticles showed cytotoxicity against cancerous cells via ROS generation. TiO2 and ZnO nanoparticles and their composites have been synthesized by chemical route. Their structural properties indicate the anatase phase of TiO2 while ZnO formed has shown hexagonal wurtzite structure. The SEM images showed that TiO2 NPs are formed in very small and uniform spherical morphology while ZnO formed in the form of small nanorods. The band gap and ROS generation of TiO2 reduces when it's composite has been made with ZnO nanorods.

**Keywords:** Titanium dioxide, ROS generation, MTT assay

## Introduction

Metallic titanium (Ti), its oxide and alloys have been broadly applied as insert material in orthopaedics and dentistry, due to their unique characteristics, they are biocompatible, good resistor to decay, less dense, and more strength [**1-3**]. On the other hand, due to quite bio inert, titanium, titanium dioxide and its composites are normally encapsulated by rubbery tissue in vivo and reveal the deficiency of osseo integration, which can bring to the infections. A sterilized surroundings of implant is role in precautionary the infections, consequently, the antibiotics cure is frequently practical after implant surgical procedure [**4**]. But, delivery of antibiotics in a systematic ways is not absolutely way to achieve the goal the infection domain, and the trauma of surgical implant can decrease the resistance of body against infections. For that element, disease due to bacteria may direct to cause of breakdown [5-6] Then, novel Titanium-based with their biocompatibility and antibacterial properties are necessary for superb -class implantation.

In sort to surmount the said challenge, a variety of strategy has been in use to get better the resistive of Titanium implants to disease. Which consist of Titanium coated with antibiotic/ chitosan and cyclodextrins etc. [**7**] modifying the surfaces of Titanium implant by antibiotics of covalent bond [**8**] Titanium metals coated with calcium phosphate included antibiotics [**9**] Titanium coated with biocide glass–ceramic [**10**] and to apply antibacterial agent films to Ti alloys amongst a range of strategy, incorporate antibacterial agent on the surface of Titanium implant has been become admired in current times such as, coating of Ag-modified TiO2 [11,12] copper- titanium dioxide(Cu–TiO2) coatings and coating of titanium with ruthenium complex The element Zinc (Zn) is a recognized as a trace element which creates the bones in humans, in recent times it revealed hopeful osteoblast production with action of alkaline phosphatise Zinc oxide has greater specific surface area so it generally used as a antibacterial agent. Due to its greater antibacterial action it also used with coating of biological materials. Titanium coated with zinc oxide (ZnO-Ti) reduces the growth of bacteria both germs positive and germs negative the antibacterial activity of zinc oxide (ZnO) is focused much but its method to use is still undecided. There are two theories in the present studies which are metal ion dissolution and photo catalytic The TiO2 NPs are biological materials which have greater surface area, less modulus of elasticity and matchless topography. Due to these properties TiO2 have greater contract of concentration. TiO2 NPs with convinced features are recognized to progress its biological belongings of titanium substrate, furthermore its nanostructure can provide as storing agent to create continual antibacterial activity TiO2 NPs have been recognized to produce Reactive Oxygen Species (ROS) which property uses as a antibacterial and anticancer activity in present work, we syntheses extremely planned TiO2-NPs and after that we coated zinc oxide (ZnO) on the nanoparticles by means of popular the sol–gel method. Their anticancer activity was checked on Human liver cancer cells (HepG2) through generation of reactive oxygen species (ROS)

### Experimental Details

The TiO2, ZnO are separately synthesized by the sol. gel, and co-precipitation methods, respectfully. Additionally, TiO2@ZnO nanocomposites have been deposited using two step synthesis approach, i.e., sol. gel and co-precipitation methods. Initially, the TiO2 nanoparticles are deposited using sol-gel method by using Titanium Isopropoixide (C12H28O4Ti), Nitric acid (HNO3) +Distilled water and ethanol as precursors. A mixture of ethanol (20ml) and Titanium isopropoxide (20ml) was prepared by stirring followed by the addition of 24ml distilled water into the mixture.

In order to maintain the pH of the solution, 10ml of 30% $HNO_3$ was added drop wise into the solution.

The mixed solution was stirred for 4 hours while maintaining a constant temperature of 60oC.

As a result a gel is formed which was then put into the Oven at 80oC for 10 hours for drying purpose.

This dried gel was then grinded to convert it into powder form followed by an annealing at 500oC for 2 hours to get good crystalline of the $TiO_2$ nanostructures. Further the ZnO nanoparticles were synthesized by co precipitation method.

For the purpose, 2.725 g of $ZnCl_2$ was added into distilled water to make solution of 20ml. then a sodium hydroxide solution by adding 4.8 g of (NaOH) into 30ml of distilled water. It was added drop wise into the $ZnCl_2$ solution with continuous stirring at 45oC.

After mixing the solution was stirred for 2 hours which resulted in the formation of white precipitates.

These ZnO precipitates were then separate out from the solution by centrifuge machine and washed with a mixture of ethanol and distilled water several times.

These particles were then place in a drying oven at 100oC for 24 hours followed by the grinding process.

In order to prepare ZnO and $TiO_2$ nanocomposites, the as prepared $TiO_2$ nanoparticles were added into the $ZnCl_2$ solution and repeated the same procedure as mentioned above for the synthesis of ZnO nanoparticles.

The structure of the synthesized ZnO, $TiO_2$ and ZnO@$TiO_2$ nanocomposites has been studied by the Bruker D8 Discover X-ray Diffractometer. The morphology of the particles have been analysed by VEGA3 TESCAN scanning electron microscopy. The optical nature has been studied by taking the absorbance spectra from UV-Visible spectrophotometer.

In vitro activity of synthesized NPs has been tested on HepG2 cells (Human liver cancer cells). For the purpose, MTT-based colorimetric assay was used to measure the number of feasible cells. The activity of samples was determined by measuring the absorbance light of wavelength at 570 nm, which is proportional to the number of living cells.

## Results and Discussion

For morphology of the synthesized nanostructures, every material has been scanned for SEM images and shown in Figure 1.

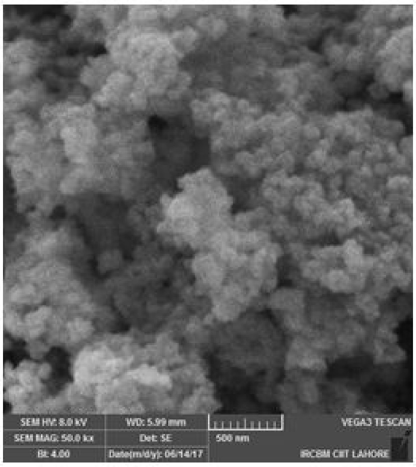


**Figure 1a.** SEM image of $TiO_2$ nanoparticles

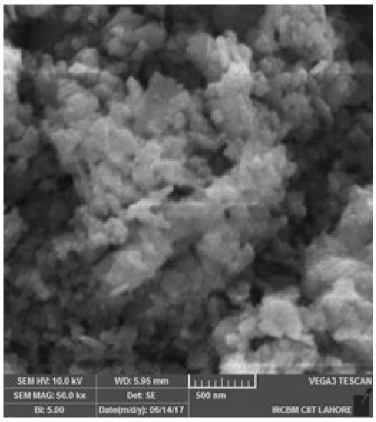


**Figure 1b.** SEM image of ZnO nanoparticles

We can see in the figure 1a that $TiO_2$ nanoparticles are formed in the shape of small circular particles with average size up to 100 nm in diameter. This morphology is uniform and has been seen for all $TiO_2$ particles in the sample. In the second micrograph (figure 1b) the morphology of ZnO nanostructures has depicted. These nanostructures are seen to have columnar growth pattern with a non-uniform rod length. The average diameter of these nano-rods is found to be around 40 nm. There have been so many broken and agglomerated nanostructures are also visible in the ZnO micrograph. The SEM image for the nano-composite sample shows various nanostructures spreading on a nonuniform big agglomerated particle. In Figure 1c, it can be seen that it contain small particles along with the nano-rods, which suggest that $TiO_2$ and ZnO particles have maintained their individual shape in the prepared nanocomposites as well as compared to when they prepared in the single sample form.

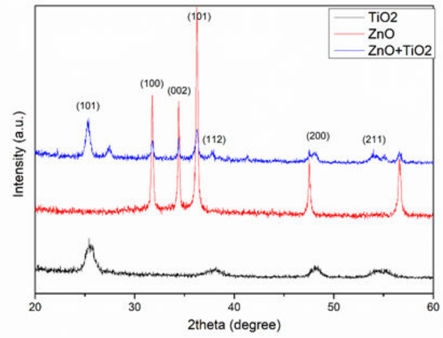



**Figure2:** X-ray diffraction patterns of TiO2, ZnO and their nanocomposites

The x-ray pattern for TiO2, ZnO and then ZnO@TiO2 nanocomposites are shown in the figure 2 The black curve in the figure that corresponds to the TiO2 nanoparticles demonstrates the anatase type of crystal structure as referenced by the JCPDS card no. 21-1272. The characteristic diffraction peaks for anatase TiO2 crystal structure\ are exhibited at 25.40o, 38.06o, 48.19o and 53.90o that are corresponding to the (101), (004), (200) and (211) planes, respectively. The second curve plotted in red corresponds to the ZnO nanoparticles that have been synthesized separately. It can be seen that this XRD spectrum exhibits the hexagonal wurtzite structure of ZnO has been in good agreement with the JCPDS card no. 36-1415. The structure has confirmed by the characteristic peaks at angles 31.70o, 34.45o, 36.19o, 47.50o and 56.60o indexed to (100), (002), (101), (102) and (110) planes, respectively. When ZnO nanoparticles are on the TiO2 particles then both structures exhibit their characteristic peaks in the third curve confirming that in the ZnO@TiO2 nanocomposites both the structures have maintained their individual identity. In addition, the crystallite sizes of each sample are estimated using Scherer's formula and the values are tabulated in the table 1.

**Table1:** Value of crystallite sizes estimated from Scherer's formula

| Sample | TiO2 | ZnO | ZnO-TiO2 |
|---|---|---|---|
| **Crystallite Size (nm)** | 15.03 | 37.93 | 37.99@14.45 |

The average particle size of TiO2 and ZnO generally remain same in both cases, i.e., individually and in composite form.

UV-Vis absorption measurements describe the optical properties of TiO2; ZnO and ZnO@TiO2 samples are shown in figure 3.

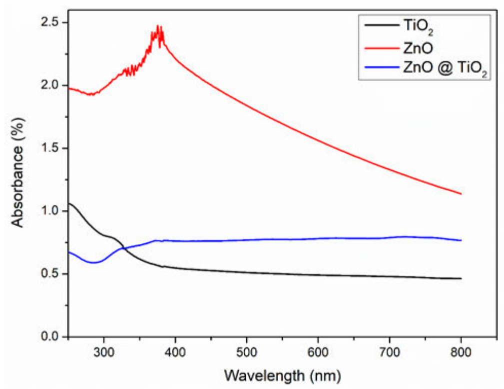



**Figure3:** Absorbance spectra of the TiO2, ZnO and ZnO@TiO2 nanocomposite.

In the figure it can be seen that ZnO shows higher absorbance in comparison to TiO2 in the visible region but with a decreasing trend toward higher wavelengths. Furthermore, when ZnO attached to the TiO2 to from nanocomposites, it again causes the rise in overall absorbance of the sample.

To calculate the band gap of all material samples, Tauc relation have been used and is plotted in the figure 4.

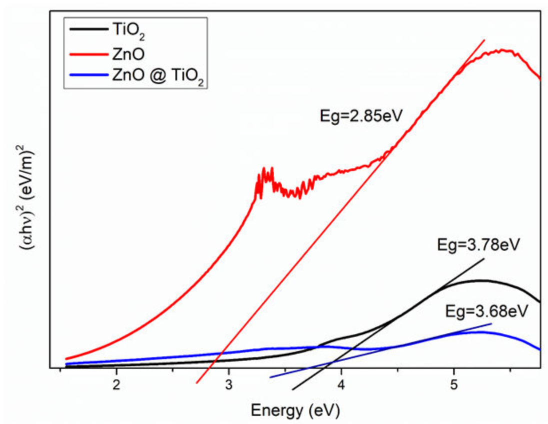



**Figure4:** Plot of (αhυ) 2 versus photon energy (hυ) of TiO2, ZnO and ZnO@TiO2 nanocomposites

The estimated band gap energies of TiO2 and ZnO nanostructures were 3.78 and 2.85 eV, respectively. But when these two materials were merged to make nanocomposites its band gap energy value become 3.68 eV which is very close to the TiO2 that was the host material in the composite.

The results for the toxicity have been presented in figure 5

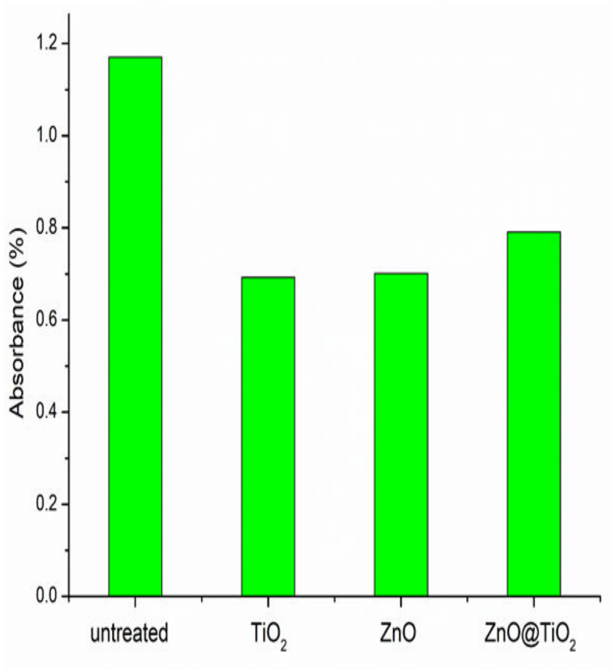



**Figure5:** Anticancer activity of Ti O2, Zn O NPs an d ZnO-TiO2 nanocomposites in HepG2 cells

Where the absorption of light by the living cells is shown in case of untreated sample (UT), and TiO2, ZnO and ZnO@TiO2 nanocomposites.

Metal oxide nanoparticles also showed their cytotoxicity against cancer cells through cellular oxidative stress.

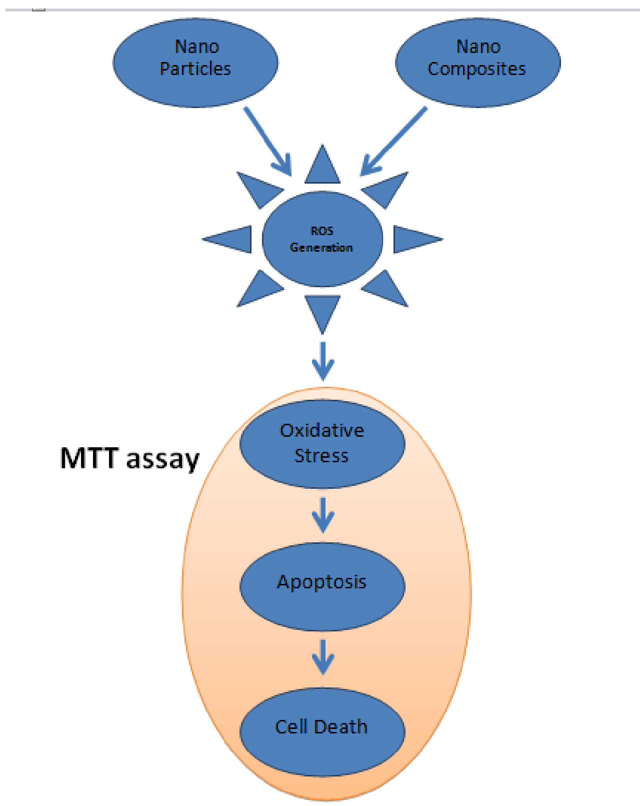
The cytotoxicity of each sample (TiO2, ZnO and ZnO@TiO2 NPs) may make sure their enhanced potentials.

There was considerable difference in cell viability of all samples groups of NPs. However cell feasibility ZnO@TiO2 was greater than naked samples.

The up-regulation of intracellular reactive oxygen species (ROS) can produce oxidative stress which may direct to apoptosis. It has earlier been confirmed that metal oxide nanoparticles can carry apoptosis in human cancer cells by ROS generatio.

To clarify the mechanism of enhanced anti proliferation effectiveness TiO2, ZnO and ZnO@TiO2 NPs, ROS-generation assay was performed in HepG2 cells.

Intracellular ROS levels were confirmed by detecting the population percentage of live cells.




The population percentage of the composite ZnO@TiO2 was significantly greater than those of Individual TiO2 and ZnO NPs. The higher ROS level of the individual TiO2 and ZnO compared with the composite ZnO@TiO2 NPs may explain the improved antiproliferation in HepG2 cells. The individual TiO2 and ZnO exhibited a larger ROS level compared with the ZnO@TiO2 NPs which may be due to their greater cellular contact and cytotoxicity stroke mechanisms. This decrease in cytotoxicity has been also observed in case when the oxide nanoparticles of one kind are covered with the second one, i.e., core shell structure, due to the less exposed surface area that may responsible for ROS generation Similar effects of toxicity reduction has been seen when SiO2 and ZrO2 were used as composite materials with TiO2 The antiproliferation potential of TiO2 and ZnO NPs was also larger than that of composites sample as shown in Figure 5. In gathering, in the case of in vivo applications, each sample may show dissimilar pharmacokinetic properties after intravenous direction. It is anticipated that individual TiO2 and ZnO NPs may make stronger in vivo anticancer behaviour via ROS generation in tumour tissues.

## Conclusion

In conclusion, the individual ZnO and TiO2 nanoparticles and their nanocomposites have been formed by using co precipitation and sol-gel methods, respectively. It was observed that the crystallite size remain almost same for the particles in individual and nanocomposites form. The TiO2 nanoparticles were formed in spherical form which ZnO got the rod shape. The optical band gap of TiO2 NPs was 3.78eV and for ZnO it value found to be 2.85eV. When TiO2 is formed with ZnO, then energy band gap value reduced to 3.68ev in comparison with pure TiO2. It was also observed that the cell viability was more in composite then pure samples which concluded that anticancer activity of composite materials was decreased. ROS was mainly responsible for the damage of cell membranes of cancer cells and it is dependent on the ion production. The reduction in the free Ti and Zn ions in nanocomposites was the main reason for the weakened toxicity. The composite formation of ZnO and TiO2 might have effectively reduced the exposed area for ROS generation and ultimately reducing the cytotoxicity of the nanomaterials for HepG2 cancerous cells.

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