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Research Article

MORPHOLOGICAL AND STRUCTURAL STUDIES OF ZnO AND TiO_2 NANOPARTICLES AND THEIR ANTIBACTERIAL ACTIVITY

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A B S T R A C T

Nanostructured Zinc oxide (ZnO) and Titanium dioxide nanoparticles (TiO_2 NPs) were synthesized successfully using the Sol-gel method. The synthesized ZnO and TiO_2 Nps were investigated by means of XRD, FT-IR, DLS, FE-SEM and HR-SEM techniques. XRD analysis confirmed the crystalline nature of ZnO and TiO_2 nanoparticles with hexagonal Wurtzite and tetragonal structure, respectively. The calculated crystallite size matched with the HR-SEM data. Using Dynamic light scattering (DLS) technique the size distribution of the average particles histogram of ZnO and TiO_2 Nps were determined. FT-IR analysis established the fundamental structure of ZnO and TiO_2 NPs. The morphology of the NPs was confirmed by the FE-SEM analysis. HR-SEM analysis reveals the spherical structure of ZnO and TiO_2 NPs with the average particle size ranging from 20-40 nm. The synthesized ZnO and TiO_2 NPs could be utilized for a variety of interesting applications. The synthesized ZnO NPs and TiO_2 NPs studied the antibacterial activity.

INTRODUCTION

Nanomaterials are a broad term that is used to explain particles in the size range of 1 - 100 nm[1]. Nanomaterials exhibit altogether peculiar properties, which make them enormously advantageous for a variety of applications in different fields[2]. Nano-range metal oxides have received significant attention due to their characteristics physical and chemical properties [3]. ZnO Nps have attracted intensive research efforts for their unique properties and versatile applications in photovoltaic solar cells[4], varistors[5], cosmetic industry, typically in sunscreens and facial creams[6], gas sensors[7] chemical sensors[8-9] biosensors[10-11]. Titanium dioxide (TiO_2) nanoparticles have found in numerous applications in Paints [12], Photocatalystic[13], UV protection agent (Sunscreen) [14], photovoltaic,[15], Sensing[16], toothpaste[17] and electrochromic as well as photo chromic applications. Their biological and optically benign properties allow them to be suitable for UV protection. Both ZnO and TiO_2 NPs are known for their photo-catalytic activity under UV-Visible light irradiation. Materially, ZnO NPs are semiconductor type particles with a band gap of 3.37 eV corresponding to the wavelength of 368 nm. Contrarily, TiO_2 NPs exhibit band gap energy of 3.18 eV. Both ZnO and TiO_2 Nps are one of the most resourceful materials considering their applications in energy generation, degradation of organic pollutants, membranes in solar cell, chemical and biological inertness, non-toxic, photo-stable and extremely simple to prepare. Depending on the particle size it may reflect crystalline nature, facilitating the reactive species to adsorb on the surface and therefore, displaying a great efficiency in a broad range of catalytic processes. ZnO and TiO_2 properties may be influenced by its surface area, crystal structure and density of surface hydroxyl groups. All these parameters could be altered by with various synthesis methods [18-24]. Among all, the sol-gel process represents the most frequently used method. The sol-gel method contains several advantages over other methods of synthesis such as low cost, chemical homogeneity, temperature and purity of the sample. However, sol-gel chemistry also suffers from significant limitation such as (i) Semi-crystalline yields are obtained which need further calcination at nanosize particles, since the present technology requires small-sized particles for possible Applications (ii) In addition extended reaction times are generally observed which may lead to Contamination of the products. Due to the outspread usage of ZnO and TiO_2 Nps water bodies end up as the ultimate sinks for these environmental contaminants.

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Experimental

All the reagents are of analytical grade purchased from Sigma Aldrich and used as received without further purification. Zinc acetate dihydrate ($Zn(CH_3COO)_2$. $2H_2O$), sodium hydroxide(NaOH), Ethanol(CH_2COOH), Titanium tetra-isopropoxide [$Ti(OCH(CH_3)_2]_4$, acetic acid(CH_3COOH), Sigma Aldrich and deionised Water.

Method of preparation

The Zno and Tio_2 nanoparticles were prepared by sol-gel method. The synthesis of ZnO nanoparticles was carried as follows: To prepare a sol, 1.4 g of zinc actetate dehydrate and 4 g of sodium hydroxide were taken. Subsequently, 5 ml and 10 ml of deionized water were measured by using measuring jar. Then 1.4 g of zinc acetate dehydrate was dissolved in 10 ml of deionised water and 4 g of sodium hydroxide was dissolved in 5 ml of deionised water. After well mixed solution, sodium hydroxide was added to the zinc acetate solution with constant stirring for about 15 minutes .The 50 ml of ethanol was added drop wise to the above the mixed solution. The synthesis of ZnO Nps includes a series of chemical reactions. The hydrolysis of zinc acetate was carried out in the presence of NaOH in ethanol to obtain ZnO colloid. The ZnO Nps are formed as a result of the equilibrium between the hydrolysis and Condensation reaction. Due to heating, zinc acetate hydrolysis to form acetate and zinc ions. The hydroxyl group of alcohol will bind with the Zn ion to form zinc hydroxide acetate, which on calcination at 450 ^{o}C for 24 h resulting in ZnO Nps [25-26].

Evaluation of bacterial activity

Antimicrobial activities of ZnO and TiO_2 Nps were evaluated using well diffusion method of ZnO on Muller-Hinton agar(MHA).The inhibition zones were reported in millimetre(mm).S.aurers and E.Coli(Gram Positive and Gram Negative) were used for the antibacterial activity. The MHA agar plates were inoculate with bacterial strain under aseptic conditions and wells (4mm Diameters) were filled with various concentration of the test compound and incubated at 37^{o}C for 24 h.

RESULTS AND DISCUSSION

XRD Analysis

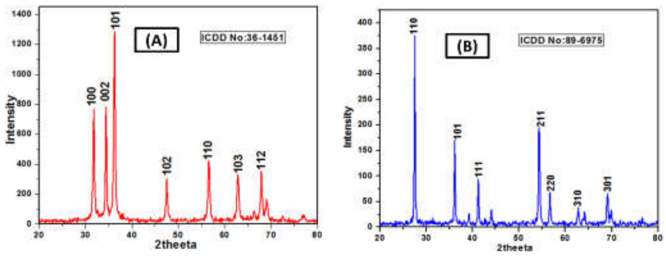


Fig 1 X-ray patterns of ZnO and TiO2 NPs synthesized by sol-gel method

In the present study, ZnO and TiO_2 nanoparticles are synthesized using the sol-gel method. In XRD analysis, 2**θ** values of 31.8, 34.6 36.2, 47.4, 56.4 , 62.7 and 67.8 assigned (100), (002) (101), (102), (110), (103) and (112) planes indicate the wurtite structure of ZnO nanoparticles (JCPDS card No.36-1451). All diffraction peaks of the sample corresponded to the characteristic Hexagonal wurtzite structure of ZnO nanoparticles. The average size of nanoparticles was 26.2 nm. The XRD analysis data confirmed the successful synthesis of TiO_2 Nps. The XRD Pattern of TiO_2 nanoparticles exhibited anatase phases of TiO_2 Nps as anatase and rutile phase. The strong diffraction peaks observed at 2**θ** position 54, 55, 63, 69, 70 were assigned to the (211), (204), (116), (220) and (215) reflection planes of the tetragonal crystal of anatase TiO_2, respectively (ICDD No.89-6975). The other diffraction peaks observed at two theta Position 27.4, 41.8 and 56.9 were assigned to the (110), (111) and (220) reflection planes of the tetragonal crystal of rutile TiO_2 The size of particles was estimated to be 30 nm according to the Debye-Scherrer formula. It is well known that the TiO_2 Nps obtained anatase and rutile phases exhibit higher photo catalytic activity under visible light.

Dynamic Light Scattering Analysis (DLS)

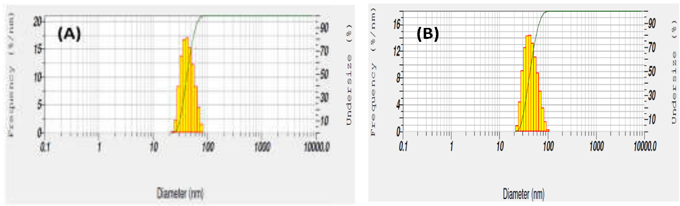


Fig 2 DLS analysis of ZnO and TiO2 NPs synthesized by sol-gel method

To confirm the size distribution of the ZnO and TiO_2 NPs, they were dispersed in deionised water, followed by ultrasonication for 30 minutes. The size distribution of the ZnO and TiO_2 Nps was determined by this analysis. The average particle size was measured by following the principle of DLS. The average value of the disturbed histogram was taken as the average particle size of the particular material. The obtained average particle sizes for ZnO and TiO_2 are 35 nm and 44 nm respectively [27].

FTIR Analysis

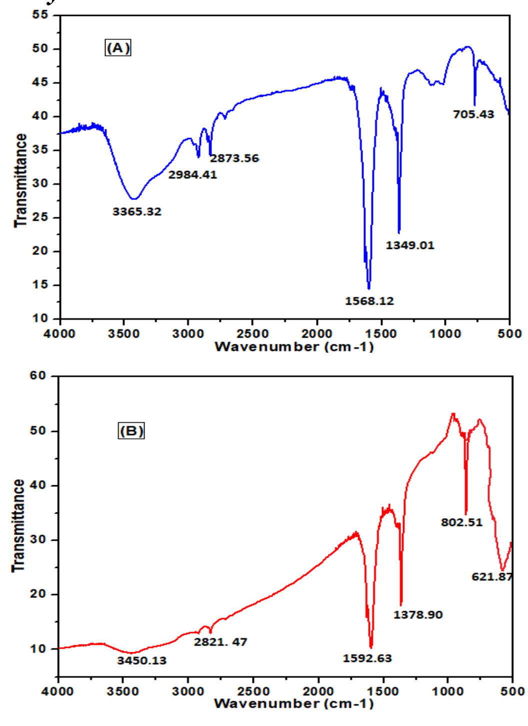


Fig 3 FTIR spectra of ZnO and TiO2 NPs synthesized by sol-gel method

The FT-IR analysis was carried out to confirm the functional groups present in the ZnO and TiO_2 Nps. From Fig A, [28-29]The stretching vibration bond from 500-700 cm^{-1} correlated to the metal oxide bond of ZnO Nps. A sharp peak at 1568.12 cm^{-1} confirms the presence of (C=O) Carboxyl functional group. A broad band at 3365.32 cm-1 corresponds to hydrogen bonding due to O-H functional group. From Fig B, a broad bond at 621 cm^{-1} is due to the bending vibrations of Ti-O-Ti bonds in TiO_2 NPs. The band between 1200-1300 cm^{-1} corresponds to the C-OH bond. The C=C bond vibrations were observed in the range of 1500-1600 cm^{-1}. A shorter band at 3450 cm^{-1} is due to the presence of hydroxyl group.

FE-SEM and HR-SEM Analysis

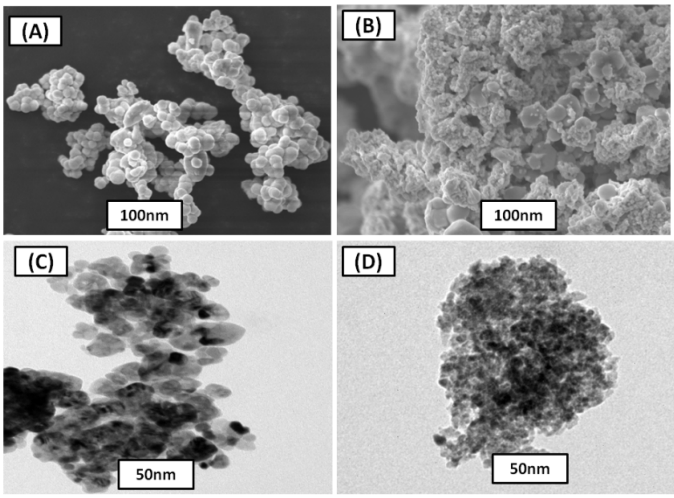


Fig. 4 FE-SEM images of ZnO NPs (A), TiO2 NPs (B) and HR-TEM image of ZnO NPs (C), TiO2 NPs (D) synthesized by sol-gel method

The Fig 4(A) represents FE-SEM image of ZnO Nps displaying spherical like morphology. The size of the ZnO Nps is in the range of 50-100 nm. The spherical like morphology consists of a bunch of spherical nanoparticles. Despite that, it is difficult to examine the surface structure of nanoparticles by FE-SEM image and therefore it was examined by HR-TEM analysis. The nanoparticles combined with each other, strongly supporting the formation of spherical like nanostructure of nanoparticles. The size of ZnO nanoparticles was found in the range of 100 nm. Fig. 4(B) displays the FE-SEM images of synthesized TiO_2 under sol-gel method, where the particles are large and agglomerated with irregular spherical structure. HR-TEM analysis was performed to recognize the particle distribution and estimate the size of the particle, which was then compared with crystallite size obtained from XRD. Fig 4(D) represents the HR-TEM images obtained for the TiO_2 sample prepared with the sol-gel method. Particles are distributed evenly and the nanoparticles are in the size range of 100 nm, the particle had an average size of 24 nm. The obtained Crystallite size values from XRD complement very well with HR-TEM values [30-31].

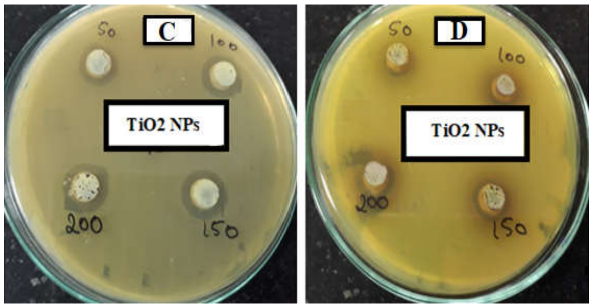


Fig 5 Effect of ZnO NPs and TiO2 NPs on gram positive and gram negative bacteria

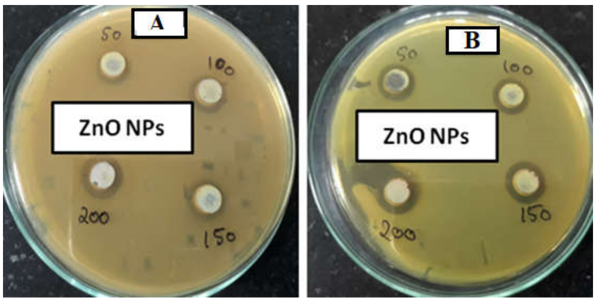
Several Studies revealed the capability of metal oxide Nps as alterative compound to antibiotics due to good germicidal activity. The antibacterial activities of ZnO and TiO_2 Nps are shown in the (Fig 5). The E.Coli and S.aureus were inoculated in MH medium with various concentrations of ZnO and TiO_2 Nps.Mainly the growth of E.coli and S.aureus inhibited compared to the low concentrations and the results inversely proportional with increasing the concentration of ZnO and TiO_2 Nps. Show the effect of ZnO and TiO_2 Nps on S.aureus in high concentration. The number of studies on the germicidal mechanisms of ZnO and TiO_2 Nps connecting to release of positively charge ions to reaction media associated to thiol group of the proteins on the cytoplasmic membrane.This reaction arrests the cell wall and increased permeability next to it, cause to collapse the structure of cellular components such as DNA, ribosomes and Cellular enzymes and to conclude the death of microorganism cell [32].

CONCLUSION

Zinc oxide (ZnO) and Titanium dioxide (TiO_2) nanoparticles (Nps) were synthesized through Sol-gel method. The results of the XRD and TEM showed that the average particle of ZnO and TiO_2 Nps nearby coincide size of the particles, and the FE-SEM results showed that the formation of spherical shaped of ZnO and TiO_2 Nps. Furthermore, the FTIR showed that the a broad absorption band related to Zn-O and Ti-O-Ti stretching vibration band. The ZnO and TiO_2 Nps showed the good antimicrobial activity on gram positive and gram negative bacteria

Table 1 Zone of inhibition of gram positive and gram negative bacteria affected by ZnO NPs and TiO2 NPs

S. No.	Compounds	Zone of inhibition (Diameter in mm at conc. 3mg/mL)							
		ZnO and TiO2 NPs							
		Klebsiella pneumoniae (-ve)				*Staphylococcus aureus* (+ve)			
		50 µl	100 µl	150 µl	200 µl	50 µl	100 µl	150 µl	200 µl
1.	**ZnO NPs**	6 ± 0.7	10± 0.34	10 ± 0.27	13 ± 0.29	8± 0.18	9± 0.17	12 ± 0.22	14± 0.31
2.	**TiO2 NPs**	8± 0.29	9± 0.35	12± 0.22	14 ± 0.91	6± 0.26	8± 0.23	9 ± 0.27	13 ± 0.19



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