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HYDROTHERMAL SOL-GEL SYNTHESIS OF TIO_2/ ZNO NANOPARTICLES

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ABSTRACT

In the previous decade, nanoparticles made up of a combination of different materials gained widespread attention. This is due to the fact that the physical, electronical, optical, or catalytic capabilities of nanoparticles arising from inorganic crystalline, glassy, or metallic qualities may be employed for the material tailoring in addition to the molecular inorganic-organic hybrid network. Titanium oxy-(1, 2-pentadione) and zinc acetate were used in a hydrothermal sol-gel process to create titanium zinc oxide nanocomposites free of potentially harmful fillers. We used an X-Ray Diffractometer (XRD) and a Scanning Electron Microscope (SEM) to examine the composites after they were formed to find the best conditions for nanoparticle generation, the reactions were carried out at 90°C and 180°C for varying amounts of time.

Keywords: *Zinc, Nanocomposites, Metal oxide, Titanium dioxide, Distilled water*

I. INTRODUCTION

The synthesis and characterization of titanium dioxide (TiO2) and zinc oxide (ZnO) using the sol-gel method have garnered significant attention in recent years due to their wide range of applications in various fields. The sol-gel method is a versatile and promising technique for producing nanostructured materials with tailored properties, making it suitable for synthesizing TiO2 and ZnO nanoparticles with enhanced functionalities. These metal oxides exhibit unique physical, chemical, and optical properties that have led to their application in photocatalysis, sensors, electronics, energy devices, and biomedical fields.

The sol-gel method is a solution-based approach that allows for the controlled growth of nanoparticles with high purity and tunable properties. The process involves the formation of a sol, a colloidal suspension of nanoparticles in a liquid phase, followed by gelation to obtain a solid network. The sol-gel method offers several advantages, such as low-temperature processing, the possibility of doping with different elements, and the ability to obtain nanoparticles in various shapes and sizes.

TiO2 and ZnO are wide-bandgap semiconductors with unique characteristics that make them attractive materials for a broad range of applications. TiO2 is well-known for its exceptional photocatalytic properties, which enable it to degrade pollutants, purify water, and generate hydrogen through water splitting under ultraviolet (UV) irradiation. Additionally, TiO2 is used in self-cleaning surfaces, anti-fog coatings, and solar cells. ZnO, on the other hand, exhibits excellent electrical and optical properties, making it suitable for optoelectronic devices, sensors, and piezoelectric applications. Furthermore, ZnO's biocompatibility has led to its exploration in various biomedical applications, such as drug delivery and bioimaging.

The sol-gel method offers significant advantages for the synthesis of TiO2 and ZnO nanoparticles, particularly in tailoring their size, morphology, and crystal structure. The ability to control these parameters allows for the optimization of their properties and performance in specific applications. Furthermore, the sol-gel method enables the incorporation of various dopants to modify the band structure and enhance the photocatalytic and electronic properties of the nanoparticles. This level of control is crucial for developing efficient and cost-effective nanomaterials for real-world applications.

In recent years, the quest for sustainable and environmentally friendly materials has intensified, leading to a strong interest in TiO2 and ZnO nanoparticles as eco-friendly alternatives for various industrial processes. Their photocatalytic activity, especially under visible light, has shown promising results in the degradation of organic pollutants and the disinfection of water. Moreover, the ability of TiO2 and ZnO nanoparticles to generate reactive oxygen species under light irradiation has sparked interest in their use as antibacterial agents, thus addressing the global challenge of antimicrobial resistance.

Overall, the synthesis and characterization of TiO2 and ZnO nanoparticles using the sol-gel method have demonstrated great potential for a wide range of applications. The unique properties of these metal oxides, coupled with the tunability provided by the sol-gel method, have opened up new avenues for developing advanced nanomaterials with improved performance and efficiency. As research in this area continues to progress, the applications of TiO2 and ZnO nanoparticles are expected to expand further, making significant contributions to various technological, environmental, and biomedical challenges of the modern world.

II. SOL-GEL METHOD FOR NANOPARTICLE SYNTHESIS

The sol-gel method is a versatile and widely employed technique for synthesizing nanoparticles and nanostructured materials. This approach involves the conversion of a liquid precursor solution, known as a sol, into a solid gel network through controlled chemical reactions. The process begins with the preparation of a precursor solution containing metal alkoxides, metal salts, or other metal-containing compounds. Subsequently, a hydrolysis reaction takes place, where water molecules react with the metal precursors, leading to the formation of metal hydroxides. These metal hydroxides then undergo a condensation reaction, where they form oxide bonds with each other, resulting in the formation of a three-dimensional network. The aging of the gel further enhances its structural integrity, and subsequent drying removes the solvent, yielding a solid nanoparticle precursor. Finally, calcination is performed at elevated temperatures to remove organic components and promote the crystallization of the nanoparticles. The sol-gel method offers several advantages, including the ability to tune the size, morphology, and properties of nanoparticles by adjusting various synthesis parameters. It enables the production of nanoparticles with high purity and homogeneity in a single-step process, making it suitable for large-scale applications. Additionally, the sol-gel method is

compatible with doping, allowing for the incorporation of different elements to modify the nanoparticles' functionality. Due to these advantages, sol-gel synthesized nanoparticles find applications in diverse fields such as photocatalysis, sensors, optoelectronics, energy storage, and biomedical applications, making it a promising route for the development of advanced nanomaterials.

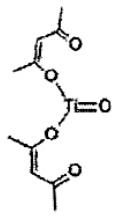
III. METHODOLOGY

Materials

Methanol, distilled water, titanium oxy-(1,2-pentadione) (99%), zinc acetate (99%), and zinc oxide (99%). No additional purification of the reagents was necessary because they were all of analytical grade.

Synthesis of TiO_2 -ZnO nanoparticles at 90^{O}C and 180^{O}C

In order to complete the synthesis, the following steps were taken: With constant stirring, 0.67g of titanium oxy (1, 2- pentadione) was poured into 5ml of distilled water. After that, 5 ml of methanol was added to the aforesaid combination. Another beaker had 0.33g of zinc acetate dissolved in 5ml of distilled water, to which 5ml of methanol was then added. Afterwards, the two solutions were combined at room temperature and transported to a Teflon-lined stainless steel autoclave (Fig. 1). Finally, clean glass slides were put in the autoclave and kept level during the hydrothermal process. The electric oven was preheated to 90 degrees Celsius, and the reaction time was set between six and twelve hours. Everything was done again, this time at 180 degrees for six and twelve hours for comparison. There is an equation for the outcome of the reaction, and it looks like this:



$$+ \quad \text{H-OH} \qquad (OR)_3\text{-Ti-OH} + \text{ROH} \qquad \text{(hydrolysis)}$$

$$(OR)_3\text{-Ti-OH} + (OR)_3\text{-Ti-OH} \qquad (OR)_3\text{-Ti-O-Ti-}(OR)_3 + \text{H-OH} \qquad \text{(condensation)}$$

In the same way that zinc acetate can be used to create zinc oxide, zinc oxide networks can also be synthesised using the same synthetic routes. Aggregation occurs when there is a buildup of -Ti-O-Ti- bonds, which causes the bonds to start interlacing and eventually form a gel.

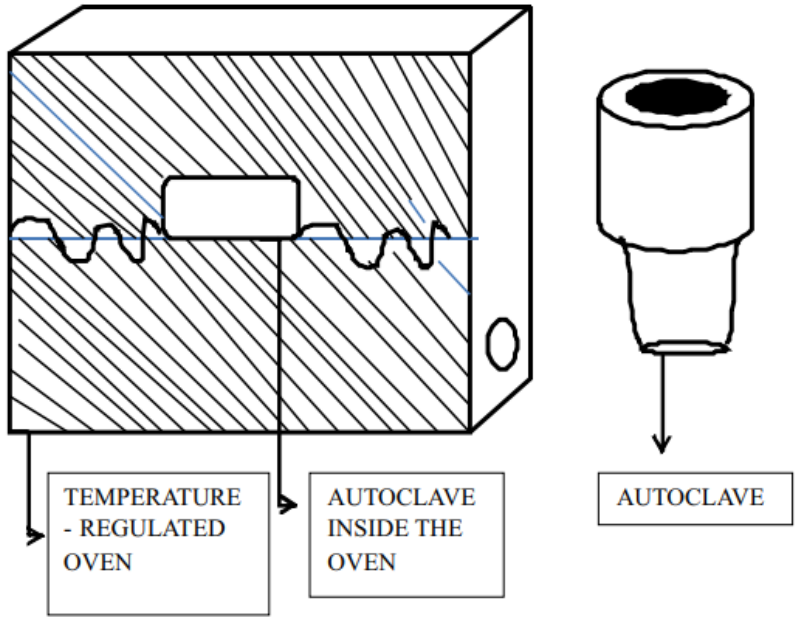


Figure 1: Hydrothermal Set-up

Characterization

Energy-Dispersive X-ray spectroscopy was used to determine the elemental make-up of the sample. With the help of a scanning electron microscope, we were able to determine the shapes and dimensions of the synthesised products. Java-based imaging software called imageJ was used to process the images and calculate particle sizes. The samples were prepared for SEM examination by being mounted on copper grids that had been coated with a holey carbon support film. Crystallite sizes were determined using the Sherrer equation, and X-ray diffraction patterns were obtained using a Rigaku D-max 2200 diffratometer with CuKa radiation.

IV. RESULTS AND DISCUSSION

Elemental Compositional Analyses

To get both qualitative and quantitative data on each element present in the sample, an energy dispersive X-ray spectrometer was used to determine its elemental composition (Fig. 2 & 3). Different parts of representative grains were scanned to generate spectra indicating the presence and relative abundance of each element in the sample. Titanium, zinc, and oxygen, the three elements that make up titanium dioxide and zinc oxide, were all detected in the spectra of the prepared sample. Both the coating and the apparatus contributed to the carbon and silicon found. Titanium (mean weight and atomic percentage: 32.40, 14.92), Zinc (mean weight and atomic percentage: 14.76, 4.94), and Oxygen are the primary ingredients. Titanium to zinc was determined by EDX to have a stoichiometry of 2:1, which is consistent with the ratio found in the precursors.

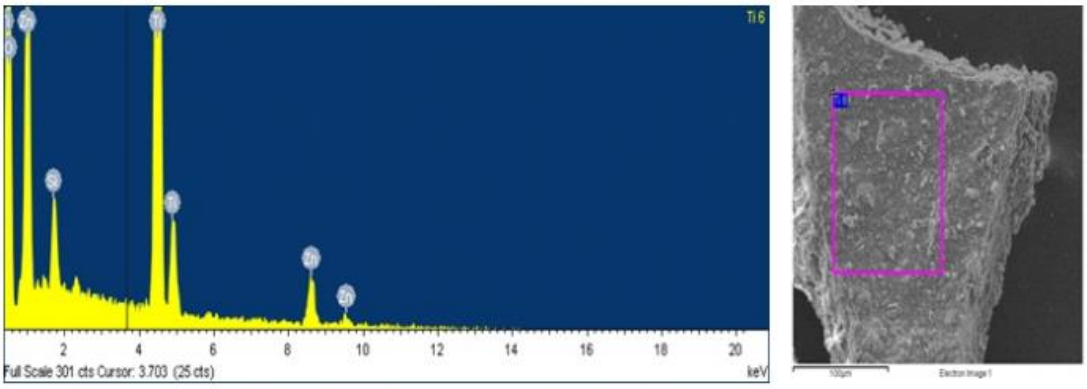


Figure 2: Spectrum of Energy Dispersion of a Representative Grain

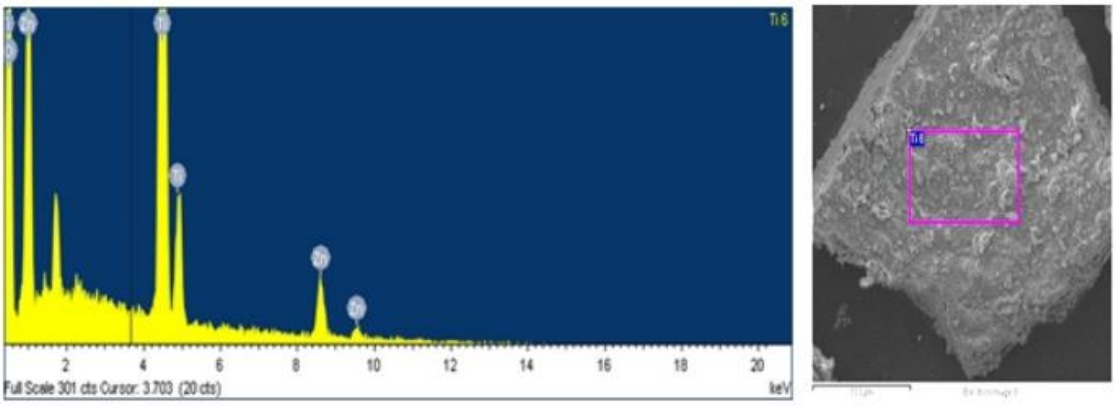


Figure 3: Representative Grains' Energy Dispersive X-Ray Spectra

X-Ray Diffraction Results

Studies at lower temperatures 200 ^{o}C using the same methods led to the formation of TiO2 and ZnO composites, but at higher temperatures >500OC for sol-gel methods, three major compounds of the type ZnTiO (spinel ortho-titanate), Zn_2TiO_4 (perovskite meta- 3 titanate), and Zn_2TiO_8 (cubic) were produced.

Titanium oxide (Ti_3O_5), rutile phase titanium dioxide (TiO_2), and zinc acetate hydrate were all included in the product obtained from O synthesis at 90 C for 6 and 12 hours, as shown by the X-ray diffraction pattern (Fig. 4). This demonstrated that zinc acetate does not hydrolyze at this temperature, and that, according to phase diagram equilibria, there is no way for zinc acetate molecules to become incorporated into the crystal lattice of the titanium dioxide. Both narrow and broad peaks in the XRD pattern indicated that the particles in the mixes fell into the micro- and nano-particle size ranges, respectively.

Titanium dioxide (anatase) and zinc oxide nanocomposites develop at 180°C and maintain their diffraction spectra for 6 and 12 hours [Fig.5]. TiO_2 (anatase) has the distinctive diffration oooo o peaks at 2Θ = 26.5^{o}, 36.5^{o}, 38.5^{o}, 48.5^{o}, and 55.5^{o}, whereas ZnO shows peaks at 31.8 ^{o}, 34.4 ^{o}, 47.7 ^{o} and 56.9 ^{o}.

It is likely that the tiny dimensions of the crystallites were responsible for the observed anomalies in the peaks and the modest shift of the peaks to higher 2Θ values than those described in the literatures for TiO2

andZnO. Using the Sherrer equation, we may estimate that the average crystal size at 180O C is between 44 and 70 nm.

$$T = \frac{K\lambda}{B\cos\Theta}$$

Where K is the particle factor (particle factor is 0.9 if the shape is spherical), B is the peak half-width, Θ and λ are the incident angle and X-ray wavelength of 0.152nm respectively.

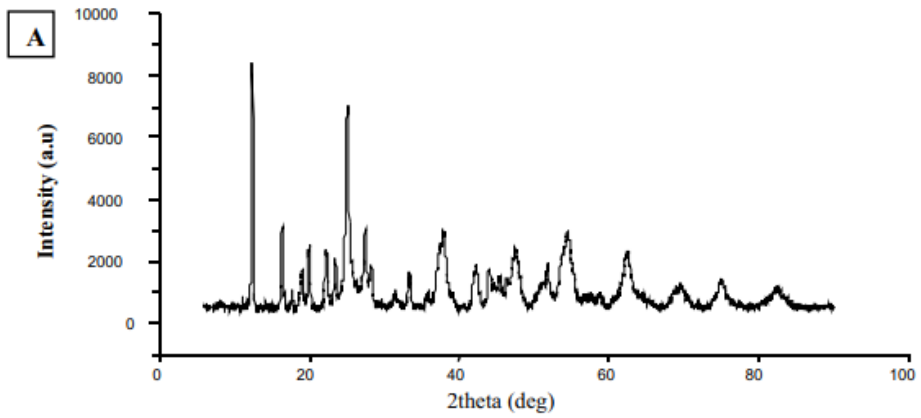


Figure 4: XRD Spectrum of TiO_2-$Zn(OOCCH_3)_2$ at 90°C

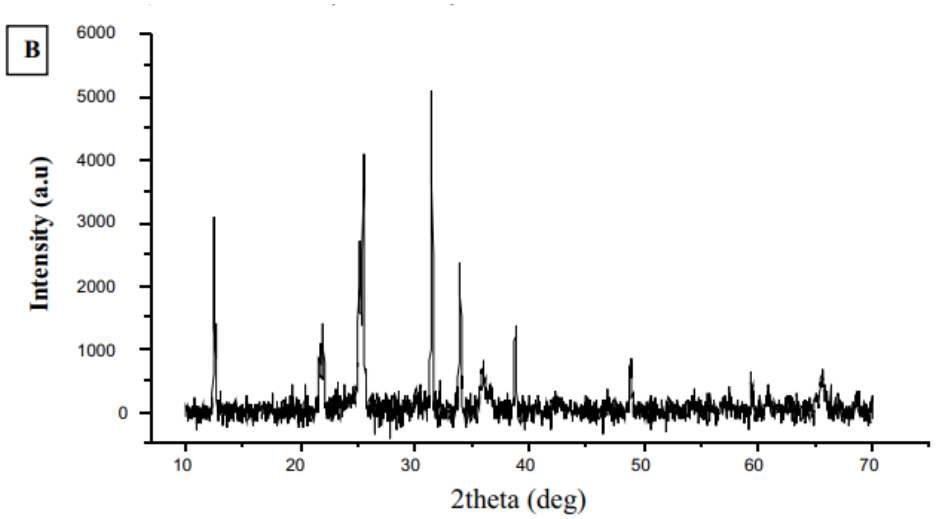


Figure 5: XRD Spectrum of TiO_2 -ZnO at 180 °C

Scanning Electron Micrograph Images

The XRD result indicated formation of TiO2 /Zn(OOCH3)2 at a preparation temperature of 90°C (Fig. 6), and the corresponding SEM image revealed a zeolite-like topography with well-defined cages of 2-3 m and chanel thickness of 174-387nm. Perhaps the water molecules trapped in the zinc acetate lattice evaporated, resulting in the intriguing cage and channel topology.

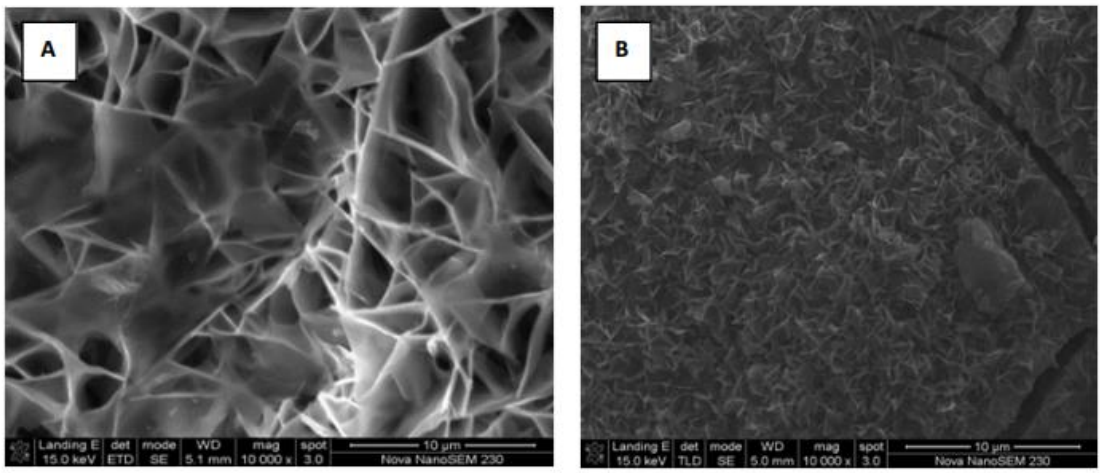


Figure 6: SEM Images of TiO_2 /$Zn(OOCCH_3)_2$ Mixtures Prepared at 90°C at Low Magnification (A) 6hrs (B) 12hrs

Micrographs of the composites taken with an SEM at 180°C show that the original nanoparticles coagulated to form flake-like bigger grains, which resemble crumbled cookies (Fig. 7), in contrast to the SEM images taken at 90°C. The diameters of the original nanoparticles, 49-90nm as determined from the x-ray diffraction pattern, are planar spheres.

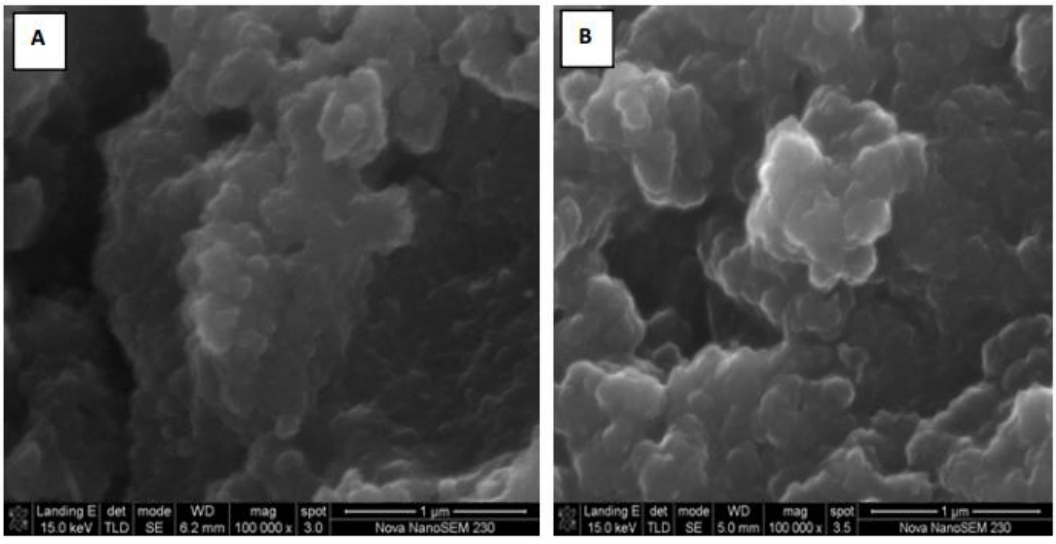


Figure 7: SEM Images of Representative Product at 180°C for (A) 6 and (B) 12 hrs

V. CONCLUSION

Zircon flour, fly ash, and aluminium metal are all readily available and may be used to create MMO nanoparticles using the sol-gel technique. While the titanium oxy- (1, 2-pentadione) O precursor allowed for effective TiO2 /ZnO nanocomposites synthesis at 180°C, the zinc acetate's inability to hydrolyze to the appropriate zinc oxide at 95°C resulted in cage-like topology for the composites. Titanium dioxide and zinc oxide did not create chemical bonds, as seen by the X-ray diffraction pattern, but instead formed composites with particle sizes between 70 and 180 nm, which agreed with the SEM results. Images showed the development of coagulates that were both spherical and flat on their surfaces.

REFERENCES: -

1. Parashar, Mritunjaya & Shukla, Vivek & Singh, Ranbir. (2020). Metal oxides nanoparticles via sol–gel method: a review on synthesis, characterization and applications. Journal of Materials Science: Materials in Electronics. 31. 10.1007/s10854-020-02994-8.

2. Sharma, Malti & Pathak, Mallika & Kapoor, Pramesh. (2018). The Sol-Gel Method: Pathway to Ultrapure and Homogeneous Mixed Metal Oxide Nanoparticles. Asian Journal of Chemistry. 30. 1405-1412. 10.14233/ajchem.2018.20845.

3. Prasad., A.J.K., "Development and Comparative Studies of Polymer Composites Reinforced with Nano Ceramic Oxide Powders", in Mechanical Engieering. 2012, Visvesvaraya Technological University: Siddaganga Institute of Technology. p. 39.

4. Perkgoz, N. K., Toru, R. S., Unal, E., Sefunc, A. Tel, S. Mutlugun, E. Soganci, I. M., Celiker, H. Celiker, G. and Demir, H. V.2011. Photocatalytic hybrid nanocomposites of metal oxides nanoparticles enhanced towards the visible spectral range. Applied Catalysis B: Environmental (Elsevier).105:77-85

5. Prasad, A.J.K., Shashidhara. S M., and Muralidhara B.K.,, "Synthesis and characterization of mixture of nano zirconia and nano silica obtained from commercially available zircon flour by sol-gel method". Bulletin of Materials Science, December 2011. Vol. 34, No. 7 pp 1339.

6. Qu J, Luo C, Hou J. Synthesis of ZnO nanoparticles from Zn-hyper accumulator (Sedum alfredii Hance) plants. IET Micro Nano Lett. 2011;6:174–6.

7. Chitralekha, K., Mishra, M.K, and Ashu R,, "Synthesis and characterization of fly ash supported sulfated zirconia catalyst for benzylation reactions". Fuel Processing Technology October 2010. 91(10): p. 1288-1295.

8. R. Y. Hong, J. H. Li, L. L. Chen, D. Q. Liu, H. Z. Li, Y. Zheng, J. Ding, “Synthesis, surface modification and photocatalytic property of ZnO nanoparticles”, Powder Technology, 189, 426–432, 2009.

9. T. V. Mclaren, G. Solis, S. C. Li Tsang, “Shape and Size Effects of ZnO Nanocrystals on Photocatalytic Activity”, Journal American Chemical. Society, 131, 12540– 12541, 2009.