

**SURFACTANT – FREE, FACILE SYNTHESIS OF ZINC TUNGSTATE
NANOPARTICLES FOR PHOTOCATALYTIC, ANTIBACTERIAL AND
HUMIDITY SENSING APPLICATIONS.**

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ABSTRACT: *Synthesis of surfactant - free zinc tungstate (ZnWO₄) nanoparticles was carried out by co-precipitation technique. The synthesized ZnWO₄ nanoparticles were characterized by powder X-Ray Diffraction (XRD) for phase analysis, Scanning electron microscopy (SEM) for morphology, Dynamic light scattering (DLS) for particle size analysis, Ultra-violet absorption spectra for optical properties. The photocatalytic ability was analyzed using synthesized ZnWO₄ nanoparticles as photocatalyst for the degradation of an organic dye – Rhodamine B (Rh B) under visible light source. The degradation efficiency was above 95% which evident the degradation of the Rh B dye solution. The antibacterial activity of the synthesized nanoparticles was assessed against the gram-positive and gram-negative bacterial strains. Staphylococcus aureus and Escherichia coli were under analysis which shows prominent zone of inhibition. The humidity sensing ability was measured using synthesized ZnWO₄ nanoparticles at different relative humidity ranges. It exhibits the sensitivity factor of 1411 with quick response and recovery characteristics.*

Keywords: *ZnWO₄ nanoparticles, Photocatalyst, Antibacterial activity, Humidity sensor.*

I. Introduction

Nanotechnology had been the area of enthrallment for the researchers as it grasps the modern innovations in the field of science and technology. Nanotechnology dealing with particles of particle size in nanometer range paves towards miniaturization of devices and compatibility. The nanoparticles find application in the environmental, sensing, medical, optical, communication and electromagnetic fields. The synthesis of these nanoparticles was carried out using enormous methods which was the underlying factor responsible for its size, morphology and functioning in assorted applications. Among the nanoparticles, the metal tungstates withhold its sturdy position in scientific field. Transition metal tungstates were the exorbitant research material due to its robust properties thereby paving way to technological applications. Their exorbitant physical and chemical properties initiate them applicable in the numerous fields. In particular, Zinc tungstate (ZnWO₄) was known to possess ornate physico-chemical properties. There were various techniques of the synthesis of the ZnWO₄ nanoparticles such as sol-gel, hydrothermal, microwave assisted method, co-precipitation, solid state reaction. Amongst which the eco-friendly, economic, simple and user-friendly approach was the requisite characteristics for its efficient application in various sectors. The chemical stability of zinc tungstate leads to its ample applications; widely as humidity sensor, hydrogen sensor and photocatalyst [1-3].

Now-a-days, the major crisis on environment was due to the water pollution. The majority of contaminants, impurities in the water bodies were the dyes from industrial effluents. These contaminants affect the living being due to its adverse impact on ground water thereby causing health issues and affecting the suave survival of aquatic as well as terrestrial lives. Photocatalysis had been the solution for the removal of dye contamination from water, as it was cost effective and environmental friendly approach. The redox reactions of the photocatalysis process degrade the dyes without leaving any secondary pollutants to the environment. Metal tungstates, in particular ZnWO₄ have been known to possess the photocatalytic property [4, 5]. With the improvement in the field of science and technology, a major attention was

necessitated to the health sector of the society due to the infectious diseases caused by multidrug resistant microorganisms. Bacterial infections were the serious issue; not only causing illness, but also affecting the processing in food, textile, medicine and several industries. Nanoparticles have been known to have the antibacterial properties against several gram-positive and gram-negative species that was attributed to its size. Nanoparticles have properties that differ from the bulk materials due to its surface-to-volume ratio. Among the bacterial strains, the antibiotic-resistant, multidrug resistant (*Staphylococcus aureus*, *Escherichia coli*) pathogens are the area of research interest, as the infections caused by them are more complicated to treat [6, 7]. Following the health sector, humidity monitoring had been vivid in wide areas ranging from agriculture to medicine. The miniaturization, fabrication and production of humidity sensors were of utmost requirement. Relative humidity sensors were the preferable and commonly used due to its economic and user-friendly characteristics. The interaction between the surface of the sensing material and the water molecules shows the sensing ability of the material which was monitored by changes in the electrical measurements. Several metal oxides and nanoparticles possess sensing behavior; but there remains the need for commercial grade sensor with the high sensitivity, low response time, high accuracy and low cost material. The size and porous nature of the material greatly governs the humidity sensing ability [8-10]. Thus, the aim of the work was to synthesize material with multiple applications. In the present work – we synthesized multifunctional ZnWO₄ nanoparticles which were analyzed for its photocatalytic ability by photodegradation of rhodamine B, antibacterial activity and humidity sensing ability.

II. Experimental section

A. Synthesis of ZnWO₄ nanoparticles

Equimolar solution of zinc chloride and sodium tungstate were mixed and magnetically stirred for two hours at room temperature. The resultant white precipitate was lixiviated and calcined for two hours; that was used for further analyses. The synthesis was done in the absence of any surfactant, additives and capping agent.

B. Characterization

Powder XRD was recorded with “XPRT-PRO” for phase analysis. Surface morphology was analyzed using AU Quanta 250 FEG scanning electron microscope, the particle size was measured using Zetasizer 3000HS instrument and the JASCO V-630 spectrophotometer was used for UV-Visible spectral analysis.

C. Photocatalytic, antibacterial and humidity sensing studies

The photocatalytic ability was analyzed using photodegradation of rhodamine B (Rh B) dye solution [11]. 0.025g of the synthesized ZnWO₄ nanoparticles was taken as the photocatalyst to degrade 100 ml of the aqueous Rh B solution of concentration (2×10^{-5} M). The suspensions were stirred in dark for 30 min to make them attain the equilibrium condition. The suspensions were then irradiated by a 250w tungsten-halogen lamp as visible light source. After irradiation, the suspensions were collected at regular interval of time and analyzed for the concentration of the Rh B dye.

The antibacterial assay was carried out using agar well diffusion technique with wells tunneled using cork borer of 6mm diameter. DMSO was taken as solvent which also serves as control [12]. The synthesized ZnWO₄ nanoparticles were taken with DMSO in 1mg/ml as stock solution. The stock solution was then diluted to 25µl/ml, 50µl/ml, 75µl/ml and 100µl/ml, which were taken for the antibacterial assay. Gram-positive *staphylococcus aureus* and gram-negative *Escherichia coli* were the test pathogens that were swabbed over the agar medium. The wells were loaded with the synthesized material and maintained for incubation at 37°C for 24 hours. After which the zone of inhibition in millimeters was measured. All the tests were performed in triplicates and the resultant zone of inhibition values was measured to assess the antibacterial activity of the synthesized nanoparticles.

Anhydrous phosphorus pentoxide; saturated solutions of potassium acetate, calcium chloride hexahydrate, zinc nitrate hexahydrate, calcium nitrate tetrahydrate, sodium nitrite, ammonium chloride, barium chloride dihydrate and copper sulphate pentahydrate were placed in a closed apparatus which serves as controlled humidity arrangement with relative humidity (RH) of 5%, 20%, 31%, 42%, 51%, 66%, 79%, 88% and 98% respectively [13]. The synthesized ZnWO₄ nanoparticles were kept in each humidity environment for a couple of hours followed by which the resistivity measurements were recorded. The sensitivity factor was calculated; the response and recovery time were also analyzed.

III. Results and discussion

i) Analyses on phase, morphology, particle size and optical properties

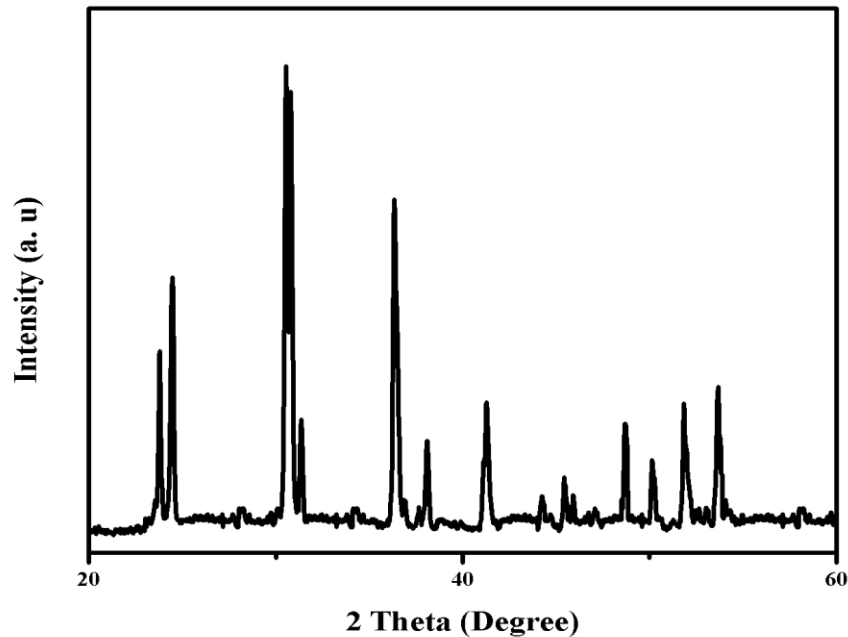


Fig. 1. Powder XRD analysis of synthesized ZnWO_4 nanoparticles

The powder XRD analysis of synthesized ZnWO_4 nanoparticles was shown in Fig. 1. It shows spiky diffraction peaks which were in accordance with the JCPDS number: 73-0554. Thus according to the JCPDS, the synthesized ZnWO_4 nanoparticles were known to possess monoclinic system with primitive lattice type and cell parameters of $a = 4.72\text{\AA}$, $b = 5.70\text{\AA}$ and $c = 4.95\text{\AA}$ with β -value of 90.08° . Hence, the synthesized ZnWO_4 nanoparticles can be described as β - ZnWO_4 nanoparticles.

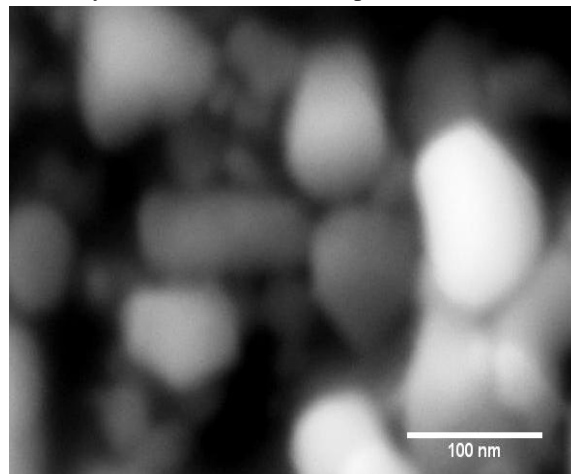


Fig. 2. SEM image of zinc tungstate nanoparticles

The SEM image of the nanoparticles was shown in Fig. 2. The SEM image shows the lopsided distribution of nanoparticles with almost spherical morphology. The particles are seen to be congregated with size less than 100 nm; the absence of surfactant/capping agent during the synthesis process may be the reason for this morphological characteristics. Further, the particle size analysis using DLS shows the polydispersity of particles and the intensity percentage was greater between 10 nm to 190 nm. The highest intensity peak was recorded at 59.3 nm as given in Fig. 3. The optical property investigated by UV-absorption spectra was shown in Fig. 4. The absorption edge was at 327 nm and the band gap value was calculated using the formula $E_g = 1240/\lambda$, where λ is the absorption edge [14]. The calculated band gap value was 3.79 eV.

This wider band gap facilitates defect related transitions, thereby increasing its potential towards applications in adsorption mechanism.

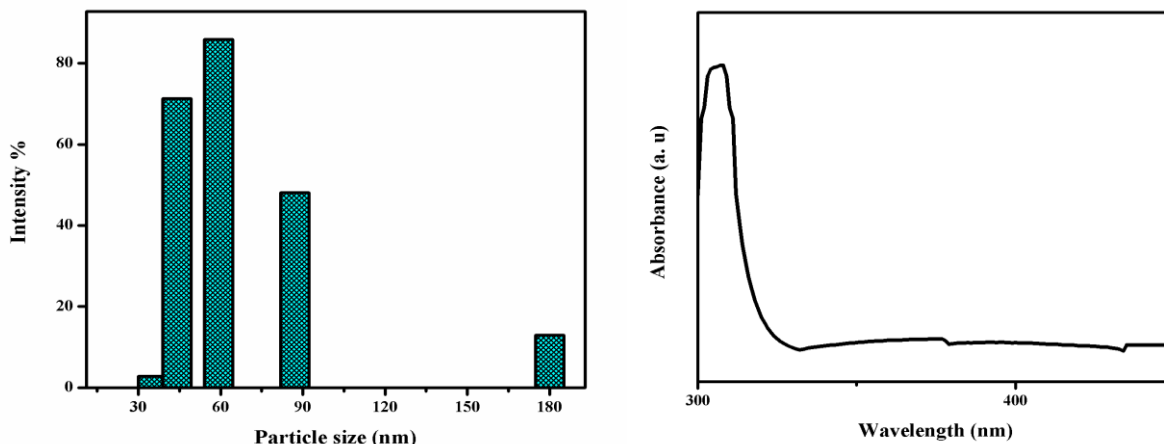


Fig. 3. Particle size analysis of ZnWO₄ nanoparticles. Fig. 4. UV-absorption spectroscopy of ZnWO₄ nanoparticles.

ii) Photocatalytic activity of zinc tungstate nanoparticles

The photocatalytic activity of the synthesized ZnWO₄ nanoparticles against Rh B dye was demonstrated under visible light. The photodegradation of Rh B was clearly observed from the plot in Fig. 5. The concentration of the dye decreases with increase in irradiation time.

The plot of C/C₀ versus time was given in Fig. 6. This explains that the degradation in the absence of synthesized photocatalyst was not possible and the Rh B was not photodegraded automatically in the absence of any photocatalytic material. But, the degradation in the presence of ZnWO₄ nanoparticles shows decrease in the concentration of the Rh B with increase in time. The degradation efficiency was calculated using the formula,

$$\text{Degradation efficiency} = [(A_0 - A) / A_0] \times 100$$

Where, A₀ is the initial concentration of the Rh B dye and A is the concentration of the Rh B dye after 60 minutes [15].

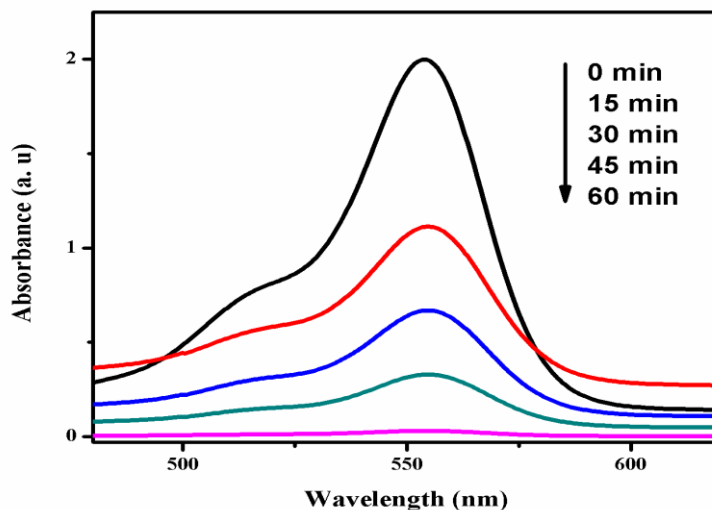


Fig. 5. Photocatalytic degradation of Rh B by ZnWO₄ nanoparticles.

The degradation efficiency after 60 minutes was found to be 98.48%. The degradation efficiency exhibited by the synthesized ZnWO₄ nanoparticles was more than the values reported by X. Zhao and G. Huang et al.,. The degradation by the synthesized photocatalyst was staggering and the mechanism/processes in the degradation of Rh B were significantly via the decomposition of conjugated ring system in Rh B molecule. As there was no significant hypsochromic shift; the de-ethylation would not be the dominant process in the photodegradation reaction. Thus, the adsorption of the nanoparticles on the Rh B dye molecules; thereby facilitates the electro-oxidation/redox reactions producing free radical species followed by its attack

towards the decomposition of conjugated chromophores were concluded to be the steps mainly involving in the photodegradation of the Rh B dye [16, 17].

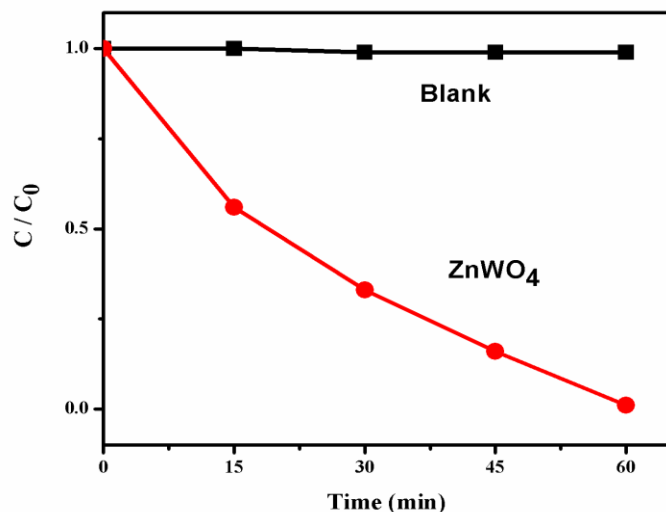


Fig. 6. Degradation in the presence and absence of photocatalyst

iii) Antibacterial activity of ZnWO₄ nanoparticles

The antibacterial activity of the synthesized ZnWO₄ nanoparticles exhibits the antibacterial assay against both gram-positive and gram-negative species as shown in Fig. 7. The zone of inhibition measured after 24 hours shows prominent antibacterial activity even with the minimum amount of the concentration of the synthesized nanoparticles. There was no prominent zone of inhibition observed for the pure DMSO solvent which was taken as control. Thus, the antibacterial activity was completely due to the synthesized ZnWO₄ nanoparticles under study and the action of the solvent against the bacterial growth / inhibition was nil.

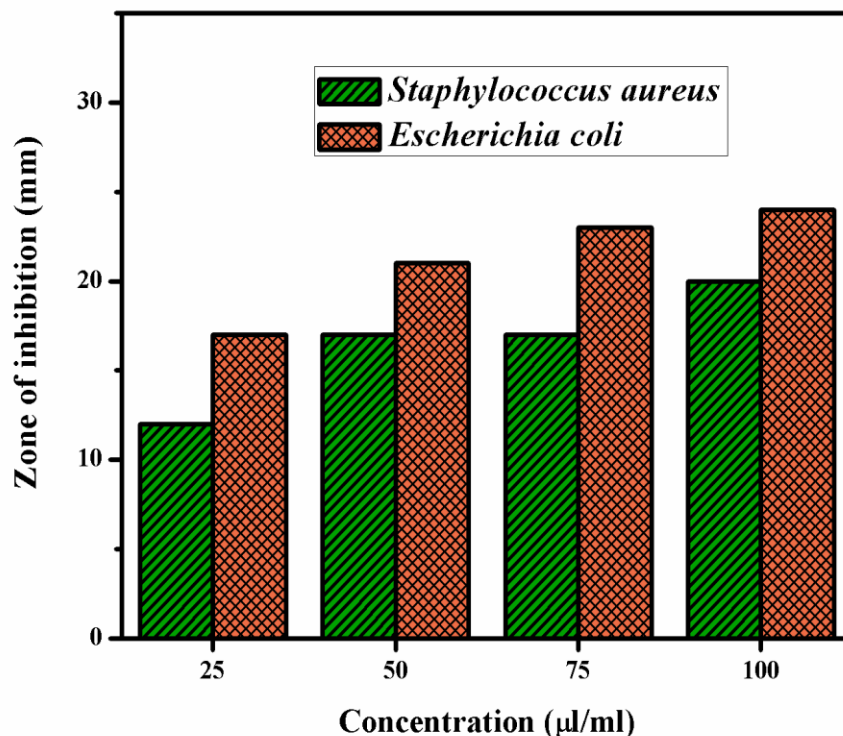


Fig. 7. Antibacterial activity of ZnWO₄ nanoparticles.

The antibacterial activity of the synthesized ZnWO₄ nanoparticles was examined to increase with the increase in the concentration of the nanoparticles. The bacterial resistivity of the ZnWO₄ nanoparticles was attributed to the biological mechanism involving at cellular level. On comparing the zone of inhibition, the zone of inhibition was greater in the case of gram-negative species (*Escherichia coli*) than the gram-positive species (*Staphylococcus aureus*). This variation in the zone of inhibition may be due to the presence of thick layer of peptidoglycan in the gram-positive species; which restricts the ease of interaction of nanoparticles at cellular level. As the gram-negative species possesses thin layer of peptidoglycan, there occurs easy interaction between nanoparticles and bacterial cell. There may be adsorption of the nanoparticles on the surface of the bacterial cell, redox reaction thereby causing interruption in the cell metabolism that would probably resulting in inhibiting the bacterial growth, causing cell damage or even death of the bacterial cell [18, 19].

iv) Humidity sensing behavior

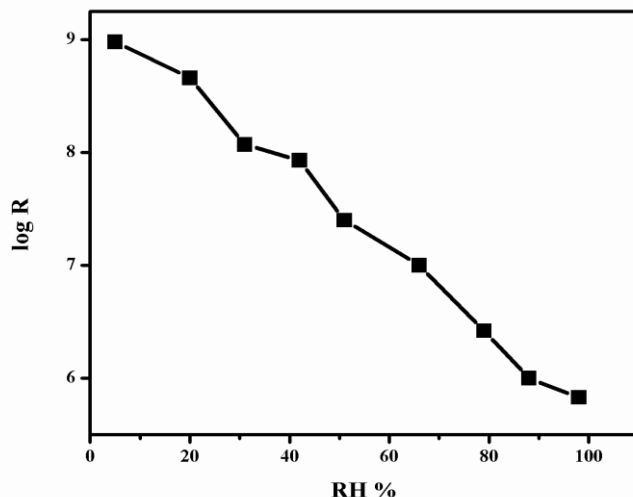


Fig. 8. Log value of Resistivity against relative humidity

The humidity sensor studies of the synthesized ZnWO₄ nanoparticles analyzed in the relative humidity range of 5% to 98%; shows the respective resultant resistance values. The graph of log R versus RH% explains the humidity sensing report. As the relative humidity increases, the log R values drops consistently as shown in Fig. 8.

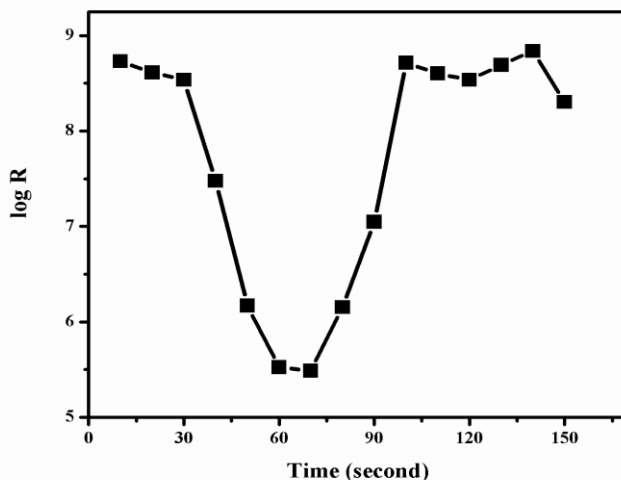


Fig. 9. Response and recover characteristics of Zinc tungstate nanoparticles.

The sensitivity factor (S_f) of the synthesized ZnWO₄ nanoparticles was calculated using the ratio of $R_{5\%} / R_{98\%}$, where $R_{5\%}$ and $R_{98\%}$ are the DC resistances at 5% and 98% of relative humidity respectively. The calculation shows the sensitivity factor of 1411. The adsorption interaction between the water molecules and the nanoparticles; the condensation via the microscopic pores between the nanoparticles facilitates the humidity sensing capability of the synthesized nanoparticles. However, the particle size, porosity, morphology and the synthesis methodology greatly influence the sensitivity and its mechanism of

action [20]. The fast response and recovery characteristic was required factor for good and commercial grade of sensor. The response and recovery characteristic was investigated with the synthesized ZnWO₄ nanoparticles as shown in Fig. 9. The response characteristic of the synthesized nanoparticles was analyzed as 30 s which exhibits the adsorption behavior of the synthesized ZnWO₄ nanoparticles with respect to time. Similarly, the recovery characteristic was 100 s which shows the desorption behaviour of the synthesized nanoparticles. The response and recovery time was seemed to be quick with prominent sensing capacity.

IV. Conclusion

The synthesized ZnWO₄ nanoparticles were known to be in accordance with JCPDS number and the morphological analysis showed the almost spherical particles with minor huddles. The particle size analysis shows that the synthesized nanoparticles were nano-ranged with most of the particles at the size range of 59 nm. The wider band gap of 3.79 eV can be attributed to be responsible for adsorption efficiency in photocatalytic as well as humidity sensor applications. The photocatalytic degradation of Rh B by the synthesized ZnWO₄ nanoparticles shows significant results. The degradation efficiency of 98.48% within 60 minutes was noteworthy, as it proves the photodegrading ability of the organic dye – Rh B by the synthesized nanoparticles. Further, the bacterial resistivity of the synthesized nanoparticles against the gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*) species was observed with maximum zone of inhibition against gram-negative (*Escherichia coli*) species. The humidity sensing behavior of the synthesized ZnWO₄ nanoparticles possesses sensitivity factor of 1411 with fast response and recovery time period of 30 s and 100 s respectively. These analyzed characteristic regarding the relative humidity makes the synthesized ZnWO₄ nanoparticles an efficient humidity sensing material. Thus, the synthesized ZnWO₄ nanoparticles can be known as cross-functional material as these nanoparticles were efficient towards photocatalytic, antibacterial and humidity sensing applications.

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