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Antibacterial Properties of F-Doped ZnO Visible Light Photocatalyst

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Antibacterial properties of F-doped ZnO visible light photocatalyst

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HIGHLIGHTS

• F doped ZnO nano-powders were obtained by a modified sol–gel method.
• These materials were found to be effective against S. aureus and E. coli.
• Enhanced visible light photocatalytic and antimicrobial properties were obtained.
• The toxic effect of ZnO on bacteria can be due to the release of zinc cations.
• Production of reactive oxidation species influences bacterial viability.

GRAPHICAL ABSTRACT

ABSTRACT

Nanocrystalline ZnO photocatalysts were prepared by a sol–gel method and modified with fluorine to improve their photocatalytic anti-bacterial activity in visible light. Pathogenic bacteria such as Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) were employed to evaluate the antimicrobial properties of synthesized materials. The interaction with biological systems was assessed by analysis of the antibacterial properties of bacteria suspended in 2% (w/w) powder solutions. The F-doping was found to be effective against S. aureus (99.99% antibacterial activity) and E. coli (99.87% antibacterial activity) when irradiated with visible light. Production of reactive oxygen species is one of the major factors that negatively impact bacterial growth. In addition, the nanosize of the ZnO
1. Introduction

Environmental pollution has become one of the major problems in developing and developed countries around the world. Traditionally sedimentation, coagulation or methods based on adsorption, have been used in treatment of industrial wastes. However, due to a number of drawbacks these methods often do not meet requirements of stringent quality standards [1–3]. As a result, in recent years continuous efforts have been made to develop innovative technologies in order to remediate polluted environment. Among them, photocatalysis serves as an attractive tool due to its efficiency and relatively low cost [4]. Currently the most widely used and studied photocatalyst is titanium dioxide (TiO2). However, several studies have reported that zinc oxide (ZnO) can also serve as a suitable alternative, mainly due to its low cost and the ability to absorb a larger fraction of the solar spectrum than TiO2 [5–7].

Zinc oxide (ZnO), a wide band gap semiconductor (3.37 eV), has a vast range of applications which include but are not limited to photocatalysts [8], varistors [9,10], pharmaceutical products [11], and lasers [12]. As a photocatalyst, in the presence of UV radiation, ZnO facilitates production of reactive oxygen species (ROS) on its surface [13]. During photocatalysis, the initial reaction starts with UV radiation of the semiconductor. Light with photonic energy greater than the band gap of a semiconductor metal oxide (e.g., ZnO), can excite an electron from the filled valence band (VB) to the empty conduction band (CB). This excitation of electrons from VB to CB results in the formation of an excited electron (e−, CB)—positive hole (h+, VB) pair. The e− CB can reduce oxygen from the surrounding environment to form superoxide radicals (O2−•) and then, with the aid of hole (h+ VB), singlet oxygen (1O2) can be formed. The h+ VB can also react with water to produce hydroxyl radicals (•OH), hydrogen peroxide (H2O2), or protonated superoxide radical (•HO2). Hydrogen peroxide can further react with •OH radicals to form •H2O2 [14,15]. The reactive oxygen species (ROS) such as •OH, 1O2, O2•−, O3, H2O2 can cause decomposition of bacteria through various actions [16,17]. In biological systems, antimicrobial action of ROS is achieved by lipid peroxidation of the cell membrane and subsequent inactivation of the microorganisms [18]. As the antimicrobial activity of ZnO has also been observed in the absence of light, it is thus assumed that production of ROS is not the only mechanism of its activity and other factors such as the impact of Zn2+ ions could play an important role [16].

It is known that by modifying the band gap, the photocatalytic properties of ZnO can be changed and tailored to a specific application. For example doping with low concentration of fluorine can significantly improve its photocatalytic activity in visible light, increase the mobility of ROS carriers and hence enhance the antimicrobial activity of ZnO in environments void of UV radiation [18]. Although the antimicrobial property of ZnO has already gained significant attention [19–21], its photocatalytic activity in visible light still requires improvement. The aim of this investigation was therefore to synthesize fluorine-doped nanoparticulate ZnO powder via a sol–gel route and to explore the effect of this process on ZnO with respect to its antimicrobial activity against selected pathogens under visible light conditions.

2. Materials and methods

2.1. Preparation of nanopowders

All reagents for synthesis were purchased from Sigma–Aldrich. A sol–gel method was used for the synthesis of ZnO and fluorinated (F-doped) ZnO with varying molar ratio of trifluoroacetic acid (TFA) was used as the precursor. In a typical experiment, zinc acetate dihydrate (10.9 g) was mixed with absolute ethanol (300 ml) at the temperature of 75–78 °C (mixture A). Simultaneously, oxalic acid dihydrate (12.6 g) was dissolved in ethanol (200 ml) at room temperature (mixture B). For the fluorination to take place, TFA was added during the preparation of mixture B (mixture F–B) in an adequate amount: 3.8 ml and 7.68 ml for ZnO:TFA 1:1 and ZnO:TFA 1:2, respectively. Unmodified nanopowders were synthesized by combining mixtures A and B only. The obtained xerogels were dried at 80 °C for 24 h and next calcined at 500 °C for 2 h in the air. There have been three batches of powders prepared in order to evaluate the reproducibility of the ZnO synthesis. The phase composition of obtained powders evaluated by XRD did not change between batches. The elemental concentrations were not found to be varied from synthesis to synthesis.

2.2. Characterization

X-ray Diffraction (XRD) analysis was performed using Siemens D-500 X-ray Diffractometer, in the diffraction angle range (2θ) between 20° and 80°, with CuKα radiation source. Particle size (L) was calculated using the Scherrer equation:

\[ L = \frac{k\lambda}{\beta \cos \theta} \]

where \( L \) = crystallite size [nm], \( k \) = constant related to the crystal-lite shape, \( \lambda \) = X-ray wavelength [nm], and \( \beta \) = full width at half maximum of a peak in radian located at any 2θ in the pattern [22].

Infrared spectra were collected using a Spectrum GX Spectrometer to identify functional groups present in nanopowders. Morphology of the nanopowders was analyzed using Scanning Electron Microscope (Hitachi SU-70) operating at 20 kV. X-ray photoelectron spectroscopy (XPS) was performed using ThermoVG Scientific Theta Probe spectrometer using monochromatic Al Kα radiation (photon energy 1486.6 eV). All spectra were charge referenced against the C1s peak at 285 eV to correct for any charging effects during data acquisition. Quantitative surface chemical analyses were calculated from the high resolution, core level spectra following the removal of a non-linear (Shirley) background. The Avantage software was used which incorporates the appropriate
sensitivity factors and corrects for the electron energy analyzer transmission function. The BET surface areas of the heat-treated (500 °C) samples were carried out using a Micromeritics Gemini ® VII V3.03 surface area analyzer operating at liquid nitrogen temperature after degassing the samples for two hours at a temperature of 200 °C. UV–vis diffuse absorbance spectra of the samples were taken using a PerkinElmer Lambda 900 UV–vis absorption spectrophotometer in the range of 300–600 nm.

2.3. Microbiological evaluation

Gram-positive *Staphylococcus aureus* (ATCC 6538) and Gram-negative *Escherichia coli* (ATCC 25922) were chosen to conduct the pure culture studies. First, sterile 10 ml aliquots of Nutrient Broth (Oxoid) and Columbia Broth (Difco) were inoculated with *E. coli* and *S. aureus*, respectively, and incubated overnight at 37 °C. Next, they were centrifuged, washed with phosphate buffered saline (PBS) and their concentration was adjusted accordingly.

In order to evaluate the effect of ZnO nanopowders on the selected bacteria, 2% (w/v) suspensions of nanopowders in M-H broth were prepared. The effect of F-doped ZnO nanopowders on the activity of *E. coli* and *S. aureus* was determined by evaluating the growth of the cultures in the presence of photocatalysts (ZnO:TFA 1:1 and ZnO:TFA 1:2), compared with the growth of the culture in medium. Unmodified ZnO nanopowder (ZnO–SG) served as the reference material. M-H broth inoculated with bacteria only served as a positive control. All solutions were prepared using aseptic methods. For test, wells of sterile polystyrene plates were filled with 5 ml of previously prepared solutions. Next, bacterial suspensions were added and the final concentration in each well was adjusted to approximately 10^5 colony-forming units/ml (CFU/ml). The prepared systems were divided into two groups: one was exposed to the source of incandescent-A light (150 W Tungsten Halogen with emission spectrum presented in Fig. 1) and another left without light access for a total period of 6 h. For further evaluation, samples from both groups were taken at 0 h, 0.5 h, 1 h, 3 h and 6 h. From the obtained bacterial culture aliquots, serial dilutions in PBS were prepared and the number of viable cells (CFU/ml) was evaluated using the pour plate technique. For the microbiological evaluation, samples were tested in triplicate.

3. Results and discussion

An ethanolic solution of zinc acetate was added to an ethanolic solution mixture of oxalic acid and trifluoroacetic acid, which produced a thick semi-gel. Subsequent drying at 80 °C in an oven produced a dried xerogel, which was then calcined at 500 °C to produce a free flowing nanopowder. There have been three batches of powders prepared in order to evaluate the reproducibility of the ZnO synthesis.

XRD was employed to determine the phase composition and the crystalline size of synthesized ZnO nanopowders. Fig. 2 shows the XRD plots of unmodified and F-doped material. All tested samples were crystalline and their phase composition was indexed as hexagonal-wurzite type ZnO, with characteristic peaks occurring at 32°, 35°, 37°, 48°, 57°, 63° and 68° according to standard PDF card (JCPDS/ICDD 36–145). The average crystalline size estimated from the Scherrer equation was 24±5 nm. The phase composition of obtained powders evaluated by XRD did not change between batches.

The results of SEM observations presented in Fig. 3 show that the obtained nanopowders were agglomerated.

The results of the FTIR analysis (Table 1) performed on dried xerogel and calcined powders are presented in Fig. 4. The spectrum of ZnO precursor dried at 80 °C revealed bands at ~3500 cm⁻¹ contributed to the presence of –OH stretching bonds [24]. Moreover, another distinct band originating from C–H bonds has been observed at 2936 cm⁻¹ and symmetric and asymmetric stretching bands of acetate species at 1658 cm⁻¹, 1319 cm⁻¹ (ν(CO2⁻)), and 815 cm⁻¹ (σ(CO2⁻)) [23]. After calcination at 500 °C, the intensity of the bands associated with the presence of organic residue was significantly reduced and a strong peak at ~450 cm⁻¹ attributed to Zn–O bond became apparent [23,24]. It was also noted that the peak at 2936 cm⁻¹ is predominant in the pure ZnO sample compared to the F-doped samples due to the presence of unburned carbon from the precursors. This is because the addition of TFA destabilizes the zinc acetate gel-network and makes the calcination faster for the doped samples. The gel structure with little cross-linking is structurally fragile and thus collapses faster during calcination [25].

UV–vis diffuse absorbance studies of all the three samples were recorded and the band gap values were calculated. From Fig. 5, it can be seen that the wavelength was measured at 391 nm, giving a calculated band gap value of 3.17 eV for the sample ZnO:TFA 1:1. Pure ZnO showed almost same absorption features with a band gap value of 3.17 eV. However, in the case of ZnO:TFA 1:2 the band gap...
calculated is slightly lower (3.16 eV), which is not significant and is believed to be within the error limit of the measurement. A Table of wavelength measured and the band calculated are given in Table 2.

The XPS survey spectrum of undoped material (Fig. 6A) represents the pattern typical for ZnO with the O1s and Zn2p3 peaks located at 530.74 eV and 1021.39 eV, respectively [25]. In addition, the peak originating from C1s is present at approximately 285 eV in all tested samples. The spectra of the F1s region for ZnO:TFA 1:1 and ZnO:TFA 1:2 powders are presented in Fig. 6B and C. Analysis of both reveals component at 685 eV attributed to zinc–fluorine bonds [26]. From the deconvolutions of F1s region, it was found that the peaks at 684.1 and 684.4 eV are from F and the other peaks are principally just noise as the F1s peaks are relatively small. However, there is an increase in the height and area of the peak at 684 eV.

Table 3 lists surface area and pore-size data of ZnO samples.

Table 2
Band gap values of various ZnO samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavelength (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>391.2</td>
<td>3.17</td>
</tr>
<tr>
<td>ZnO:TFA 1:1</td>
<td>390.5</td>
<td>3.17</td>
</tr>
<tr>
<td>ZnO:TFA 1:2</td>
<td>393.0</td>
<td>3.16</td>
</tr>
</tbody>
</table>

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was successfully introduced into the ZnO structure and the amount of the dopant detected is proportional to the amount of TFA used (1.26 at% and 2.56 at% for ZnO:TFA 1:1 and ZnO:TFA 1:2, respectively). As the presence of oxygen is responsible for ROS production, its content was also evaluated. The analysis shows that sample ZnO:TFA 1:1 contains 43.4% of oxygen, which is higher in comparison with other powders (36.3% for ZnO and 40.5% for ZnO:TFA 1:2). As reported previously, the excess oxygen (as defects levels) can be trapped in the grain boundaries of ZnO [27]. The elemental concentrations did not vary between prepared batches.

Another major aim of this study was to perform a microbiological assessment and to evaluate if the reduced particle size and F-doping enhance the antimicrobial performance of ZnO. For quantitative microbiological evaluation the suspension test was used. Prepared 2% (w/w) solutions of nanopowders in M-H broth inoculated with pathogens were divided into two groups. One was exposed to visible light and another was left without light exposure for the total time of 6 h. A graph of a relative concentration of S. aureus and E. coli as a function of time are presented in Fig. 6. Moreover, values of log reduction in bacterial population (log Red) after 6 h of experiment are presented in Table 5. The results show that antimicrobial effectiveness of synthesized powders depends on the microbial system, light conditions, and the type of materials used. In this experiment all synthesized powders showed antimicrobial properties, which was expressed by reduced bacterial population

![Graph](image-url)

**Fig. 6.** XPS spectra of the ZnO nanopowders. (A) Survey spectrum of undoped material, (B) and (C) Spectra of F1s region for ZnO:TFA 1:1 and ZnO:TFA 1:2 powders.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>C 1s</th>
<th>F 1s</th>
<th>O 1s</th>
<th>Zn 2p3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>30.40</td>
<td>0</td>
<td>36.29</td>
<td>33.31</td>
</tr>
<tr>
<td>ZnO:TFA 1:1</td>
<td>15.68</td>
<td>1.26</td>
<td>43.42</td>
<td>39.64</td>
</tr>
<tr>
<td>ZnO:TFA 1:2</td>
<td>13.73</td>
<td>2.56</td>
<td>40.46</td>
<td>43.25</td>
</tr>
</tbody>
</table>

Table 4

XPS—atomic percentage composition of the ZnO nanoparticles.
Table 5
Antimicrobial activity of ZnO nanopowders after 6h of experiment presented as log reduction (log Red). log Red = log (T0)–log (T1), where log (T0) – relative cell count at the start of experiment |log CFU/ml|, log (T1) – relative cell count after 6h of experiment |log CFU/ml|.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Control</th>
<th>ZnO 1:1</th>
<th>ZnO 1:2</th>
<th>Control</th>
<th>ZnO 1:1</th>
<th>ZnO 1:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. coli</td>
<td>0</td>
<td>1.83</td>
<td>2.88</td>
<td>1.78</td>
<td>0</td>
<td>1.74</td>
</tr>
<tr>
<td>S. aureus</td>
<td>0</td>
<td>1.43</td>
<td>4.62</td>
<td>1.95</td>
<td>0</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>Light exposure</td>
<td>Without light exposure</td>
<td>Light exposure</td>
<td>Without light exposure</td>
<td>Light exposure</td>
<td>Without light exposure</td>
</tr>
</tbody>
</table>

Fig. 7. Photographs of agar plates containing (a) Control (S. aureus), (b) Test sample (F doped ZnO 1:1, after exposure to visible light).

in comparison with controls (bacteria suspended in medium) both for E. coli and S. aureus (Fig. 7).

Results of the test performed using E. coli are presented in Fig. 8A and B. The growth of the microorganisms was the same under dark and light conditions. There was no significant change in the numbers of cells in the first hour and the numbers then increased steadily after 3 and 6h of incubation. The numbers of organisms grown in the presence of unmodified ZnO nanopowders (ZnO–SG) decreased with time for the first 3h and then remained at that level and was similar for both experimental conditions. A similar pattern of growth inhibition was obtained when the organisms were grown in the presence of F-doped powders however enhanced antimicrobial activity was observed when visible light was available. Among them ZnO:TFa 1:1 was found to be more effective in comparison with ZnO:TFa 1:2 after 6h of experiment as presented in Fig. 6A, B and Table 5 (log Red = 2.88).

When tested against S. aureus the antimicrobial performance of all powders was similar to that when the visible light was not available (Fig. 8C); however upon light exposure powder ZnO:TFa 1:1 showed superior photocatalytic activity after 1h, further reducing the number of viable cells below detection limit after 6h. These results indicate that F-doping can increase the photocatalytic activity of obtained materials. Moreover, superior antimicrobial properties of ZnO:TFa 1:1 powder can be explained by its chemical composition, as among all obtained powders it contains the highest content of oxygen (43.4%), which is believed to increase the production of ROS upon irradiation.

In the current study, the antimicrobial effect of ZnO is obvious and the number of microorganisms when contacted with nanopowders was significantly reduced when compared to the control (cultures without contact with ZnO) sample. Furthermore it was noted that among various ZnO powders used in the experiment, powder ZnO:TFa 1:1 was the most effective against E. coli and S. aureus when the visible light was available (log red 2.88 and 4.62, respectively). Based on the studies performed by others [27–31], it is believed that when the light is not available, the primary toxic effect of ZnO on microorganisms can be associated with the release of zinc ions causing disruption of the cell membrane activity and the formation of intercellular reactive oxygen species, mostly H2O2 [32–37]. Photocatalysts such as TiO2 or ZnO activated by UV or/and visible light (Fig. 9) can further generate a range of highly reactive oxygen species (ROS) such as •OH, •O2•−, •O2•H, and H2O2 [37–44] as a result of the transfer of an electron from the valence band (VB) to the conduction band (CB). The ROS produced as a result of the photocatalytic reaction will be capable of damaging the cell wall and can decompose the cellular materials (Fig. 9). It is known that the holes produced during the visible light irradiation will not have sufficient reduction potential to generate hydroxyl radical by oxidizing water molecules [5,20,41,42]. However, less oxidative species such as superoxide anions and singlet oxygen (1O2) are believed to be responsible for the anti-bacterial action during the visible light induced photocatalysis [5,20].

Padmavathy and Vijayaraghavan [31] reported that hydroxyl radicals and superoxide anion radical affect the outer part of the cellular membrane, whereas H2O2 can migrate inside of bacterial cells. Fluorine also plays an important role as it can reduce the band gap of the photocatalyst and increase its photocatalytic performance in the visible light region [38–41]. It is also evident from the studies that oxygen defects play an important role in obtaining optimum properties [40]. Therefore the antibacterial property observed for F-doped ZnO is most likely a combination of the toxic effects of Zn ions, oxygen excess defects, and the addition of F into the ZnO lattice. The anti-microbial actions of fluorine against Gram-positive and Gram-negative bacteria were also reported in Ref. [45]. Canal et al. [45] investigated the antibacterial action of Ar–CF4 treated wool, polyamide 6 and cotton fabrics using post-discharge plasma. The F radical is reported as the main active species responsible for antibacterial action against E. coli (Gram negative bacterium), S. aureus (Gram positive bacterium) and C. albicans (fungus) [45]. In a similar study, the anti-bacterial activity of diamond-like carbon coatings doped with Si and F was reported against Klebsiella pneumoniae (Gram-negative). The Si and F modified coatings reduced the bacterial adhesion by 68% at 12h compared with stainless steel [46]. A number of doped/co-doped photocatalytic materials were...
also reported [42,47–54] to show antibacterial action. However, a direct comparison of the efficiency of these catalysts is not possible due to the lack of a standard testing protocol. A comparison Table is given in Table 6.

One of the parameters that increase the antimicrobial performance is the presence of oxygen, as it takes part in ROS formation. Production of ROS is one of the factors that influence bacterial viability; however, the nanosize of the powder particles can
Aqueous Ag3VO4 ZnO TiO2 Cu

Table 6
Examples of photocatalytic materials employed for antibacterial applications.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Dopant(s)</th>
<th>Bacteria studied</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>–</td>
<td>S. aureus, E. coli</td>
<td>[42]</td>
</tr>
<tr>
<td>TiO2</td>
<td>Zn</td>
<td>S. aureus, K. pneumonia, P. aeruginosa, P. mirabilis and B. subtilis</td>
<td>[47]</td>
</tr>
<tr>
<td>TiO2</td>
<td>Cu</td>
<td>E. coli and E. faecalis</td>
<td>[48]</td>
</tr>
<tr>
<td>TiO2</td>
<td>Cu, N</td>
<td>S. aureus</td>
<td>[49]</td>
</tr>
<tr>
<td>ZnO</td>
<td>C</td>
<td>B. subtilis, E. coli</td>
<td>[50]</td>
</tr>
<tr>
<td>ZnO</td>
<td>–</td>
<td>S. aureus, B. subtilis, E. coli, K. pneumoniae, P. aeruginosa</td>
<td>[51]</td>
</tr>
<tr>
<td>ZnO:VO4</td>
<td>Ag, Mn, F</td>
<td>E. coli and E. aerogenes</td>
<td>[52]</td>
</tr>
<tr>
<td>Ag2O</td>
<td>–</td>
<td>S. aureus, E. coli, P. aeruginosa, L. fermentum</td>
<td>[53]</td>
</tr>
</tbody>
</table>

4. Conclusions

Pure and F-doped zinc oxide nanopowders were successfully synthesized by a simple sol–gel method. XPS analysis showed that fluorine doping of the ZnO structure was successful and effective. Doping of the ZnO structure enhanced the biological performance of the material, which was indicated by the improved antimicrobial properties in comparison with undoped material. Among the obtained nanopowders, ZnO:TFD 1:1 was the most effective against pathogens: S. aureus (log Red = 4.62, which is equivalent to over 99.99% population reduction) and E. coli (log Red 2.88% or 99.87%) when irradiated with light. Production of reactive oxidation species is one of the factors that influence bacterial viability. The oxygen excess defects in ZnO and possibly in other metal oxides (e.g., TiO2, SnO2, Fe2O3 or Fe3O4) can lead to an improved production of ROS and therefore the anti-bacterial and photocatalytic activity could be further improved. When the light is not available, the toxic effect of ZnO nanoparticles on bacteria can be due to the release of zinc cations causing disruption of the cell wall.

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