PVA assisted ZnO based mesoporous ternary metal oxides nanomaterials: synthesis, optimization, and evaluation of antibacterial activity

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Abstract

The poly (vinyl alcohol) (PVA) assisted highly mesoporous Zn-Fe-Mn oxides nanomaterials were synthesized using the sol-gel followed by the self-propagation techniques. The UV–vis spectroscopic technique was used to study the optical properties of the materials. The presence of metal-oxygen bond and deposited OH\(^-\)/H\(_2\)O species were characterized by FT-IR spectroscopic technique. The porous morphology and elemental analysis were confirmed by the SEM/EDX and further morphological and crystal structure studies were conducted using TEM/HRTEM techniques. The semi-crystallinity and composition analyses were verified from XRD patterns. Using the BET N\(_2\) adsorption-desorption analytical techniques; the porosity, specific surface area, and pore diameter enhancements were confirmed. The optima of PVA and precursors percentage were selected with the help of XRD, UV–Vis, and SEM techniques. The potential of the materials towards antibacterial activities was evaluated against both Gram-negative Escherichia coli and Gram-positive Staphylococcus aureus bacteria. The 50 (0.7) PVA assisted ternary metal oxide nanocomposite (PVA-TMONC) with 125 \(\mu\)g ml\(^{-1}\) concentration showed better inhibition zone for both Escherichia coli and Staphylococcus aureus bacteria, with a value of 28 and 29 mm in diameter, respectively.

1. Introduction

Over the years, antibiotics have been applied as curing agents for both Gram-positive and Gram-negative bacterial infections. Nano-biotechnology has recently gained significance in producing nanomaterial which acts as bacteria curing agent. In addition to adsorption, photocatalysis, electrochemistry, biomedical and more other applications of metal oxide semiconductors, recently their use as antibacterial treating agents has drawn attention. This is due to their high surface area, stability, biocompatibility, and possibilities of tuning to the specific morphology as needed [1]. Furthermore, this nanomaterial can also have the potential to enter through the cell membrane and distract cellular parts of the bacteria.

Among several metal oxides that are being used as an antibacterial agent, it is reported that ZnO is proven to be more abundant, low cost, biocompatible, and less toxic [2]. The general distraction mechanism of metal oxides, especially ZnO is due to the generation of reactive oxygen species such as H\(_2\)O\(_2\), OH\(^-\), and O\(_2\)\(^-\) [3, 4]. Furthermore, forming a hybrid between metal oxides can also enhance the active sites, particle size to volume ratio, polarity, and porous nature of the materials [5]. Among several metal oxides, as it is abundant, low cost, environment-friendly, thermodynamically-stable, and high surface area, iron oxides and manganese oxides are received attention. Depending on the applied temperature, among different crystalline polymorphs of iron oxide, the \(\alpha\)-Fe\(_2\)O\(_3\) phase is more stable and easy to be formed [6]. Forming a composite with Fe\(_2\)O\(_3\) and
protecting ZnO from dissolution during light irradiation were also reported [7]. And among different crystalline polymorphs of manganese oxide, the Mn$_2$O$_3$ phase shows a unique property [8].

Due to the surface area to volume ratio effect, the nanosized metal oxides are showing nobility towards antibacterial activity than bulk materials. However, due to the large surface area and high surface energy, metal oxide nanoparticles (NPs) can easily agglomerate or aggregate [9]. The classical nucleation, growth, collision, and attachment are the path to form aggregation, whereas the cluster aggregation, nucleation, and growth are the path for the formations of agglomeration. Among several methods used to prevent the agglomeration or aggregation of metal oxide NPs, nowadays, applying polymers as a capping agent has drawn extensive attention. Among several polymers, PVA is reported to be an eco-friendly, biocompatible, nontoxic, lubricant, biodegradable and safe, water-soluble, and better film-forming agent [10–12]. Furthermore, due to its good mechanical strength, PVA also used as a noble matrix for the formation of the composite [13].

As indicated on numerous works concerning PVA polymer or PVA-metal oxide composite, 500 °C is the optimum temperature to remove the unwanted impurities. On thermal analysis study of PVA, at about 100 °C–250 °C the slow intramolecular decomposition occurs. Within its melting point range of 220 °C–400 °C; the degradation of its amorphous part at ~300 °C, and the intermolecular decomposition at about 385 °C were found to occur [14, 15]. The crystalline part of PVA decays at 398 °C [16, 17], and complete decomposition to yield the carbon and hydrocarbons that led to the liberation of CO$_2$ gas and resulting in pure ZnO phase occurred in the temperature range of 400 °C–500 °C [17–19].

During the synthesis of the nanomaterials, toxic solvents, especially solvents that are suggested under severe human health risk phrases category of Global Harmonized System (GHS) Hazard and Precautionary (H&P) agency should also be taken into consideration. This is because solvents present under the category of GHS & HP are highly toxic, cancer-causing to the reproduction, and also has mutagenic properties [20].

Taking into consideration factors such as aggregation/agglomeration, stability, surface area to volume ratio, and toxicity of organic solvents; the PVA assisted ternary metal oxide nanocomposites (PVA-TMONCs) were synthesized using green sol-gel-self propagation technique. The optical properties, chemical bonding, morphology and crystal structure, crystallinity and composition, and textural properties of the materials were characterized by UV–Vis, FT-IR, SEM and TEM, XRD, and BET analysis, respectively. The antimicrobial activities of single ZnO and different ZnO based PVA-TMONCs against Gram-negative *E. coli* and Gram-positive *S. aureus* bacteria were also studied.

2. Materials and methods

2.1. Chemicals and reagents

The common analytical grade reagents used are zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) (>98%, Sigma-Aldrich), iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) (99.95%, Sigma-Aldrich), manganese sulfate (MnSO$_4$·H$_2$O, 99%, Sigma-Aldrich), poly(vinyl alcohol) (PVA) (Thermo Fisher Scientific India Pvt. Ltd, 99% hydrolyzed), and sodium hydroxide (NaOH) (98%, Oxford Lab Fine Chem LLP).

2.2. Synthesis of single and ternary metal oxides

The ZnO based PVA-TMONCs were synthesized following the sol-gel and self-propagation process. The PVA polymer was dissolved in distilled water while stirring at ~115 °C for about 15 min with continuous stirring on magnetic stirrer [21]. The purpose of using PVA is to delay cations mobility and minimizing unwanted aggregation/agglomeration of the metal oxides [22].

After cooling at room temperature, the Zn, Mn, and Fe salts were added at once to form a 0.01 mol l$^{-1}$ aqueous solution. The formed sol was aged for two days to form a gel. The gel was dried in an oven at ~110 °C. At the final drying process, the unintentional self-propagation process took place and a highly porous product was formed. After cooling and grinding, the powder was calcined at 500 °C for 3 h.

2.3. Characterization

The ultraviolet–visible spectroscopy techniques (UV–Vis) (SM-1600) in the range of 200–800 nm, Fourier transform-infrared spectroscopy (FT-IR) (Spectrum 65 FT-IR (PerkinElmer)) using KBr pellets in the range of 400–4000 cm$^{-1}$, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX-EVO 18 model with low vacuum facility and ALTO 1000 cryo attachment), transmission electron microscope and high-resolution transmission electron microscope (JEOL TEM 2100 HRTEM), N$_2$ adsorption-desorption (Quantachrome instrument), X-ray diffraction (XRD-Shimadzu X-Ray Diffractometer (PXRD-7000)) analytical techniques were used to understand the physical properties of the materials. The other common instruments used for this work include pH meter (MP 220), magnetic stirrer, hot air oven (Contherm 260 M), and furnace.
Table 1. XRD data for PVA optimization using 90, 5, and 5% of zinc, iron, and manganese salt precursors, respectively.

| Code    | PVA (g) | 2θ(°) | FWHM (radians) | Height (a.u.) | D (nm) |
|---------|---------|-------|----------------|---------------|--------|
| 100(0)  | 0       | 34.10 | 0.14723        | 11128         | 59     |
| 90(0)   | 0       | 33.64 | 0.31557        | 6812          | 28     |
| 90(0.2) | 0.2     | 34.14 | 0.26493        | 1409          | 33     |
| 90(0.4) | 0.4     | 34.14 | 0.28463        | 876           | 30     |
| 90(0.7) | 0.7     | 34.16 | 0.29477        | 1383          | 29     |
| 90(1.5) | 1.5     | 34.07 | 1.33877        | 370           | 7      |
| 90(3)   | 3       | 34.14 | 0.58477        | 887           | 15     |

Table 2. XRD data for precursor percentage optimization.

| Precursors | Code    | PVA (g) | ZNH (%) | INH (%) | MSH (%) | 2θ(°) | FWHM (radians) | Height (a.u.) | D (nm) |
|------------|---------|---------|---------|---------|---------|-------|----------------|---------------|--------|
|            | 30(0.7) | 0.7     | 30      | 35      | 35      | 40.86 | 0.93657        | 103           | 9      |
|            | 50(0)   | 0       | 50      | 25      | 25      | 34.16 | 0.20103        | 1978          | 43     |
|            | 50(0.7) | 0.7     | 50      | 25      | 25      | 42.71 | 0.86927        | 171           | 10     |
|            | 50(1.5) | 1.5     | 50      | 25      | 25      | 42.56 | 0.52567        | 269           | 17     |
|            | 70(0.7) | 0.7     | 70      | 15      | 15      | 35.34 | 0.39173        | 284           | 22     |
|            | 90(0.7) | 0.7     | 90      | 5       | 5       | 34.16 | 0.29477        | 1383          | 29     |
|            | 100(0)  | 0.7     | 100     | 0       | 0       | 34.10 | 0.14723        | 11128         | 59     |

ZNH = Zn(NO₃)₂•6H₂O, INH = e(NO₃)₉•9H₂O, and MSH = MnSO₄•H₂O

2.4. Optimization

The size of the NPs that has great effects on the antibacterial activity is dependent on the quantity of the capping agent and salt precursors [5]. The quantity of PVA and metal oxides precursors taken during optimization were given in tables 1 and 2. For PVA optimization, constant salt precursor’s percentage (zinc (90%), iron (5%), manganese (5%)) and different amount of PVA (0, 0.2, 0.4, 0.7, 1.5, and 3 g) were used and coded as 90(0), 90(0.2), 90(0.4), 90(0.7), 90(1.5), and 90(3), respectively. For percentage optimization, constant amount of PVA (0.7 g) and different precursors percentage (30, 50, 70, 90, and 100), (35, 25, 15, 5, and 0), and (35, 25, 15, 5, and 0) for Zinc, iron, and manganese, respectively were used and coded as 30(0.7), 50(0.7), 70(0.7), 90(0.7), and 100(0.7), respectively.

3. Results and discussion

3.1. Characterization

The XRD diffraction pattern of the synthesised nanomaterial that confirms the crystallinity and composition of single and PVA-TMONC materials are shown in figure 1. As seen in figure 1(a), the diffraction angles with its corresponding crystal planes appeared at ~32°(100), 34°(002), 36°(101), 47°(102), 57°(110), 63°(103), 66°(200), 68°(112), 69°(201), 73°(004), and 77°(202) corresponds to ZnO (ICSD: 00–036–1451, P63mc (#186–1)). For separately synthesized single Fe₂O₃, the diffraction angles with its corresponding crystal planes appeared at ~24° (012), 33°(104), 36°(110), 41°(113), 50°(024), 54°(116), 62°(214), and 64°(330) are indexed to hematite, α-Fe₂O₃ (ICSD: 00–033–0664, R-3c (#167–1)). Furthermore, the diffraction angles with its corresponding crystal planes appeared at ~22°(211), 33°(222), 38(004)°, 43°(332), 49°(431), 56°(440), and 64°(622) are consistent to α-Mn₂O₃ (ICSD: 24342, PBCA space group).

The particle size optimizations for PVA-TMONCs through varying PVA amount and precursors percentages were shown in figures 1(b) and (c). The diffraction pattern confirmed only the presence of ZnO semiconductor; this is due to the small percentage of Fe₂O₃ and Mn₂O₃. The XRD data (tables 1 and 2) and the respective size of the particles were calculated using Debye–Scherrer’s formula (1),

\[ D = \frac{K \lambda}{\beta \cos(\theta)} \]  

where, λ is the wavelength of X-ray radiation (for Cu 0.15418 nm), K is constant, β is the line width at half maximum height and θ is the diffraction angle.
During PVA optimization (see Table 1 and Figure 1(b)), the sharpness of the peaks for materials synthesized without PVA (100(0), ZnO (Figure 1(a)) and 90(0), (Figure 1(b))) indicates their high crystallinity. All the other PVA-TMONCs have broad and weak peaks; this may show the development of the amorphous portion on the materials. The approximate height ratio in the arbitrary unit between ZnO 100(0) and PVA-TMONC 90(1.5) is 30:1. While in between ternary composite synthesized without PVA 90(0) and PVA-TMONC 90(1.5) is 18:1. Among these, composite synthesized using 1.5 g of PVA has an average particle size of \( \sim 7 \) nm, which indicates the enhanced surface area to volume ratio. The precursor’s percentage optimization result, which is conducted using a constant 0.7 g of PVA were given in Table 2 and Figure 2(c). As seen from the data, as the percentage of iron and manganese oxide increases the particle size decreases. This indicates the potential of iron and manganese oxides towards the enhancement of the surface area. For 50(0.7) PVA-TMONC, the approximate average particle size was determined to be 10 nm.

3.2. Optical properties

The optical properties of the nanomaterials were tested using UV–Vis spectroscopic technique. As seen in figures S1(a) and (b) is available online at stacks.iop.org/MRX/7/045011/mmedia, all samples (90(0.2)–90(3) and 30(0.7)–90(0.7)) are showing a characteristic absorption maximum (\( \lambda_{\text{max}} \)) in the range of 330–350 nm. As seen in figures 2(a) and (b), the direct and indirect bandgap energy of PVA, 90(0.4) and precursor percentage, 50(0.7) antibacterial active materials were determined using Tauc plots. The equation (2) that relates optical absorption and difference between the energy of the photon and the bandgap were given as:

\[
(\alpha h\nu)^{1/n} = A(h\nu - E_g)
\]

where \( \alpha \) is the absorption coefficient, \( h \) is Planck’s constant, \( E_g \) is the bandgap, \( \nu \) is the photon’s frequency, and \( A \) is the slope of the Tauc plot in the linear region. The nature of the direct allowed/direct forbidden and indirect allowed/indirect forbidden electronic transition is dependent on the \( 1/n \) value. The 1/2, 3/2, 2, and 3 are the values for direct allowed, direct forbidden, indirect allowed, and indirect forbidden, respectively [23]. The direct
allowed transition for code 90(0.4) and 50(0.7) was determined to be 3.23 and 3.32 eV, and the indirect allowed transition is obtained to be 3.03 and 2.99 eV, respectively. As confirmed on the XRD pattern, the appearance of non-obvious change on the UV–Vis spectra is most probably due to the non-incorporation of either Fe°/Mn° or Fe³⁺/Mn³⁺ ions in the ZnO crystalline lattice [24].

3.3. Chemical bonding properties
The FTIR spectra of synthesized ZnO without PVA and PVA-TMONCs before and after calcination were given in figure 3. The broad absorption bands appeared at ~3600 and ~1650 cm⁻¹ corresponds to the stretching vibration of the chemisorbed hydroxyl groups and physisorbed water molecules, respectively. The distinctive absorption band appeared in the range of 400–650 cm⁻¹ is due to single and PVA-TMONCs. The shape, number and wavenumber position of these bands are dependent on the chemical composition, morphology, and crystal structure of the materials [25, 26]. All the other peaks that appeared can be attributed to organic impurities formed during synthesis [27, 28]. Comparing the spectra of ZnO and calcined PVA-TMONC with uncalcined PVA-TMONC one distinctive peak appeared around ~1400 cm⁻¹ is due to the -CH₂ bending of PVA, furthermore, the wavenumber shift and intensity difference were also observed. The observed shift for both calcined and uncalcined PVA-TMONC indicates surface passivation influences of PVA during synthesis. Indirectly this indicates the presence of hydrogen bond between PVA (O-H group) and metal oxides surface [10].
3.4. Morphology and microstructure properties
The morphological and microstructure properties of the materials were characterized by SEM-EDX and TEM analytical techniques. The SEM images of PVA and precursors percentage optimizations were shown in figures 4 and 5, respectively. Images have been snapped at 200 μm scale with ×70 magnification. While the inset picture on each image is snapped at 20 μm with ×750 magnification. As seen in figure 4(100(0)), single ZnO is showing agglomerated morphology. While this agglomerated property of the materials has been found to reduce moving from 0.2 to 0.7 g PVA loading as a capping agent and the porous nature of the materials was also found to increase. At 1.5 g of PVA, the flat types of morphology were observed. As seen on the XRD particle size analysis result, further increasing the amount of PVA to 3 g led to an increase in the size of the particles.

As seen the percentage optimization morphological images in figure 5, an increase in the quantity of ZnO was found to enhance the porous nature of the materials. The porous nature of the result is alike to what is observed in the synthesis process. Indicating that as the percentage of ZnO increases, the self-propagation process also enhances. The final image in figure 5 is the magnified SEM image of PVA-TMONC. The results are in agreement with XRD analysis. To confirm the presence of Zn, Mn, Fe, and O, the EDX analysis was conducted. The result showed the presence of Zn, Mn, Fe, S and O elements. The source of S is most probably from the standard used during analysis (see figure 5 EDX spectra) [29].

The NPs with the size ranging from 7–30 nm were found from the TEM image of optimized PVA-TMONC, as seen in figure 6(a). Each particle has a specific orientation attachment with its neighbors. This attachment is most probably occurred after the sample was calcined at 500 °C. During oriented attachment, the presence of fission as a driving force, the NPs found sharing a common crystallographic orientation [30–32]. As seen from

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**Figure 4.** SEM morphology for PVA optimization using constant 90, 5, and 5% of zinc, iron, and manganese salts, respectively.
the HRTEM image in figure 6(b), the obtained lattice fringes with adjacent d-spacing values of ~0.28 nm were assigned to (002) atomic plane of ZnO (inset C = magnified and D = inverse fast Fourier transmission (IFFT) pattern). The d-spacing value of ~0.34 nm is corresponding to (221) atomic plane of α-Mn₂O₃ (inset: A = magnified and B is the IFFT pattern) [33–35]. However, the lattice fringe of α-Fe₂O₃ could not be detected. This is most probably due to the higher degree of dispersed states of α-Fe₂O₃. The occurrence of stacking faults
on the IFFT pattern suggests the semi-crystalline nature of the material. The measured interplanar spacing of eight diffraction rings on SEAD pattern (0.2864, 0.2543, 0.1969, 0.1663, 0.1520, 0.1419, 0.1278, and 0.1104) clearly matches with the hexagonal wurtzite structure detected on the XRD pattern (figure 6(a) inset (A)). The diffuse ring pattern on the SEAD image indicates the presence of some amorphous regions too on the sample.

3.5. Textural properties

The total surface analysis (BET) was conducted to confirm the porous nature of the PVA-TMONC which is evidenced by the XRD pattern and SEM images. The spectra that compare the porosity enhancement from ZnO to PVA-TMONC are given in figures 7(a) and (b). Among the cylindrical, ink-bottled, and slit-shaped models, figures 7(a) and (b) appear cylindrical in shape [36–38]. Figure 7(c) compares the N₂ adsorption–desorption plots of single ZnO and PVA-TMONC. The pore size distribution of porous NPs that indicates the presence of different types of pores was expressed in terms of the Barrett–Joyner–Halenda (BJH) curve. As seen in figure 7(c) inset BJH plots, the composite shows 20–40 nm pore size distributions, indicating the mesoporous textural properties of the materials [39].
The BET surface area, \( \alpha (\text{BET}) \) were calculated from the BET adsorption isotherm equation in the linear form (equation (3)),

\[
\frac{P/P_o}{n (1 - P/P_o)} = \frac{C - 1}{(n_m C)} (P/P_o) + \frac{1}{n_m C}
\]  

(3)

where, \( P_o \) and \( P \) is saturated pressure and partial vapor pressure of N\(_2\) gas at equilibrium in pa, respectively; \( n \) is the volume of N\(_2\) gas adsorbed at STP in mL; \( n_m \) is BET monolayer capacity; \( C \) is dimensionless constant related to the enthalpy of adsorption of N\(_2\) gas on porous materials. This \( -P/P_o \) linear plots usually form a straight line within the relative pressure ranging from 0.05 to 0.3. To be acceptable, the \( R^2 \) value should not be less than 0.995. As seen in figure 7(d), the obtained \( R^2 \) value of PVA-TMONC is 0.9997. From the linear plot, \( n_m \) is calculated from \( +1 \) slope intercept, while \( C \) equal to \( \text{slope/intercept} + 1 \). Using the obtained \( n_m \) value, the specific surface area in m\(^2\) g\(^{-1}\) is calculated by the equation (4):

\[
\alpha_i = \frac{n_m L \cdot \sigma_m}{m \times 22400}
\]  

(4)

where, \( \alpha_i \) is the BET specific area of the single and PVA-TMONC of mass 0.0791 and 0.0875 g, respectively, \( L \) is Avogadro constant (6.022 \( \times \) 10\(^{23} \) mol\(^{-1}\)), \( \sigma_m \) is molecular adsorptive cross-sectional area occupied by N\(_2\) gas in the complete monolayer (is equal to 0.162 nm\(^2\) for N\(_2\) gas), the 22400 is the volume occupied by 1 mole of N\(_2\) gas at STP, in mL. The symbols used are those given in the 2007 edition of the IUPAC manual [40, 41]. The obtained average specific surface area, pore-volume, and pore diameter for ZnO is 1.5 m\(^2\) g\(^{-1}\), 0.004 cm\(^3\) g\(^{-1}\), and 9.30 nm, respectively. The improved specific surface area, pore-volume, and pore diameter for PVA-TMONC is determined to be \( \sim 24, 0.16, \) and 26, respectively. Among six types of IUPAC classification of adsorption isotherm (Type I-VI) and 4 types of adsorption hysteresis loop shape, the obtained plots look a typical IV isotherm with an H3 hysteresis loop. Being typical IV isotherm indicates the domination of mesoporous (>50.0 nm) pore size distribution and the H3 hysteresis loop indicates the presence of narrow slit pores.
4. Antibacterial activity

The antibacterial activity of selected NPs materials was carried out by the disk diffusion method and was compared to a commercial antibiotic Ampicillin. The disk diffusion test was done on Muller Hinton agar composition in (g/L). Their antibacterial activities were evaluated with three concentrations as 75, 100, and 125 μg/ml against both Gram-negative *Escherichia coli* (*E. coli*) (ATCC 25922) and Gram-positive *Staphylococcus aureus* (*S. aureus*) (ATCC 25923) bacteria. The antibacterial activity of ZnO is dependent on its particle size [42]. Compared to the PVA-TMONC (50(0.7)) that has an approximate average particle size of 10 nm, ZnO synthesized without PVA has a greater particle size of 59 nm. As seen in figure S2, ZnO (0) is not showing antibacterial activity for both Gram-negative and Gram-positive bacteria. However, all the other ZnO based composites are showing antibacterial activities. The amount of PVA and percentage of metal oxide precursor’s optimization and the respective zone of inhibition value were given in table 3. As seen in figures S2(a)–(d) of the first optimization, the bactericidal effect of NPs was found to be higher for Gram-negative bacteria than Gram-positive bacteria. As reported, this is based on the difference in the structural composition of Gram-positive and Gram-negative bacteria [43]. As seen from the result, increasing the percentage of ZnO from 10 to 30, the antibacterial activities also increases. However, further increasing the percentage to 95, the antibacterial activity is decreasing. The diameter of the zone of inhibition for 30(0.7) obtained to be 28 mm and 23 mm for *E. coli* and *S. aureus*, respectively.

On the second optimization (see figures 8(a) and (b)), further increasing the percentage of ZnO to 50%, for both Gram-positive and Gram-negative bacteria, the antibacterial activities were found to be high. The 50% of

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**Figure 8.** The antibacterial activity of synthesized PVA-TMONC (50(0.7)) towards (a) *staphylococcus aureus* (b) *Escherichia coli*.

**Table 3.** The zone of inhibitions of PVA optimization against bacteria.

| Code | Concentration (μg/ml) | *E. coli* (ZI/mm) | *S. aureus* (ZI/mm) | Code | Concentration (μg/ml) | *E. coli* (ZI/mm) | *S. aureus* (ZI/mm) |
|------|----------------------|-------------------|---------------------|------|----------------------|-------------------|---------------------|
| 0    | 75                   | 6                 | 6                   | 10   | 75                   | 6                 | 9                   |
|      | 100                  | 6                 | 6                   |      | 100                  | 11                | 12                  |
|      | 125                  | 6                 | 6                   |      | 125                  | 18                | 20                  |
| 0.4  | 75                   | 16                | 12                  | 30   | 75                   | 13                | 15                  |
|      | 100                  | 20                | 16                  |      | 100                  | 20                | 21                  |
|      | 125                  | 21                | 18                  |      | 125                  | 28                | 23                  |
| 1.5  | 75                   | 6                 | 6                   | 50   | 75                   | 13                | 17                  |
|      | 100                  | 6                 | 6                   |      | 100                  | 20                | 22                  |
|      | 125                  | 8                 | 10                  |      | 125                  | 28                | 29                  |
| Ampicillin | 125            | 22                | 20                  |      |                      |                   |                     |

*ZI* = zone of inhibition.
PVA-TMONC with 125 μg ml⁻¹ concentration had to show higher antibacterial activity against both E. coli and S. aureus. The obtained zone of inhibition in diameter for E. coli and S. aureus is 28 and 29 mm, respectively. Based on these results, it can be concluded that the synthesized PVA-TMONCs exhibited significant antibacterial action on both Gram-positive and Gram-negative bacteria. The mechanism of degradation is reported to be due to the generation of reactive oxygen species such as O₂⁻, H₂O₂, and HO·, resulting in protein oxidation, nucleic acid degradation, and disruption of biochemical processes. This enhanced antibacterial activity is due to their small size of the NPs, which provides superior contact with the surface of bacteria and penetration through the cell membrane. Moreover, the NPs deposition on the surface and their accumulation in the cytoplasm/periplasmic region also reported as a distraction mechanism that causes bacterial death [44]. Nevertheless, the release of these ions may have toxic effects. As confirmed on the XRD pattern, the nonappearance of any band position shift may indicate the absence of any structural distortion on ZnO attributed to the incorporation Fe³⁺ or Mn³⁺ ion. In advance, it may also indicate the high stability/insolubility of these metal oxides in water.

5. Conclusion

The sol-gel-self propagation synthetic method was successfully applied for the synthesis of ZnO based PVA-TMONCs. During the UV–Vis optical properties optimization process, for all different PVA and precursor quantity, the obtained λ_max value was found to be in the range of 330–350 nm. On PVA optimization using XRD, the diffraction pattern confirmed the presence of ZnO semiconductor which could be attributed to the presence of a small percentage of both Fe₂O₃ and Mn₂O₃. Moreover, the presence of those two oxides was confirmed on the EDAX spectrum. Furthermore, depending on the HRTEM lattice fringes analysis, the presence of ZnO and Mn₂O₃ were confirmed. The SEM morphology and BET analysis approve the porous nature of the synthesized PVA-TMONC. The specific surface area and pore diameter for single ZnO were determined to be 1.5 m² g⁻¹ and 9.30 nm, respectively. The respective enhanced specific surface area and pore diameter for PVA-TMONC were obtained to be ~24 m² g⁻¹ and 26 nm. The antibacterial test conducted on both Gram-positive and Gram-negative bacteria (E. coli and S. aureus, respectively) showed a good zone of inhibition, 28 and 29 mm in diameter, respectively.

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Competing interests

The authors declare that they have no conflicts of interest.

Author’s contributions

The nanomaterial’s synthesis, characterization, and first draft manuscript write up done by Buzuayehu Abebe. Sample characterization, advising, and manuscript write up improvement by H C Ananda Murthy. Further, advising and manuscript write up improvement by Enyew Zerefa. SEM optimization images characterization and antibacterial test by Yeshaneh Adimasu.

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References

[1] Dadi R, Azouani R, Traore M, Mielcarek C and Kanaev A 2019 Antibacterial activity of ZnO and CuO nanoparticles against gram positive and gram negative strains Mater. Sci. Eng. C 104 109968
[2] Pavithra K S, Yashoda M P, Prasannakumar S and Mutalik S 2020 Viscosity and thermal conductivity of ZnO–water-based nanofluids stabilized by grafted SMA-g-MPEG comb-shaped copolymer for heat transfer applications Iran. Polym. J. 29 185–96
[3] Nair S, Sasidharan A, Divya Rani V V, Menon D, Nair S, Manzoor K and Raina S 2009 Role of size scale of ZnO nanoparticles and microparticles on toxicity toward bacteria and osteoblast cancer cells J. Mater. Sci., Mater. Med. 20 235–41
[4] Sawai J 2003 Quantitative evaluation of antibacterial activities of metallic oxide powders (ZnO, MgO and CaO) by conductimetric assay J. Microbiol. Methods 54 177–82
[5] Nagvenkar A P, Deskar A, Perelshtein I and Gedanken A 2016 A one-step sonochemical synthesis of stable ZnO–PVA nanocloid as a potential biocidal agent J. Mater. Chem. B 4 2124–32
[6] Lee S and Xu H 2016 Size-dependent phase map and phase transformation kinetics for nanometric III(0) oxides (γ → ε → α) Pathway J. Phys. Chem. C 120 13316–22
[7] Qamar M T, Aslam M, Ismail M J, Sahal N and Hameed A 2016 The assessment of the photocatalytic activity of magnetically retrievable ZnO-coated c-PeO–s in sunlight exposure Chem. Eng. J. 320 1–17
[8] Yang G, Yan W, Wang J and Yang H 2014 Fabrication and formation mechanism of MnO2 hollow nanofibers by single-spinnneret electrosprinning CrystEngComm 16 6907–13
[9] Jassby D, Budarz J F and Wiesner M 2012 Impact of aggregate size and structure on the photocatalytic properties of TiO2 and ZnO nanoparticle Nanomaterials (Basel). Mater. Sci. Eng. C 32 38–43
[10] Zhang Z, Wu Y, Wang Z, Zhang X, Zhao S and Sun L 2017 Electrosprinning of Ag Nanowires/polyvinyl alcohol hybrid nanofibers for their antibacterial properties Mater. Sci. Eng. C 78 706–14
[11] Zhang Z, Wu Y, Wang Z, Zou X, Zhao Y and Sun L 2016 Fabrication of silver nanoparticles embedded into polyvinyl alcohol (Ag/PVA) composite nanofibrous films through electrosprinning for antibacterial and surface-enhanced Raman scattering (SERS) activities Mater. Sci. Eng. C 69 642–9
[12] Kumar S, Krishnakumar B, Sobral A J F N and Koh J 2019 Bio-based (chitosan/PVA/ZnO) nanocomposites film: thermally stable and photoluminescence material for removal of organic dye Carbohydr. Polym. 205 559–64
[13] Abd-Elnahaman M I 2013 Synthesis of polyvinyl alcohol–ZnO oxide composite by mechanical milling: thermal and infrared studies Nanomaterials Microscale Thermophys. Eng. 17 194–203
[14] Rahmanian R, Mozaffari S A and Abedi M 2015 Disposable urea biosensor based on nanoporous ZnO film fabricated from polysaccharide polymeric substrate Mater. Sci. Eng. C 57 387–96
[15] Radhamani A V, Sharafi K M and Rao M S R 2016 ZnO@MnO2 core–shell nanofiber cathodes for high performance asymmetric supercapacitors ACS Appl. Mater. Interfaces 8 30331–42
[16] Ghafari E, Feng Y, Liu Y, Ferguson I and Lu N 2017 Investigating process-structure relations of ZnO nanofiber via electrosprinning method Compos Part B Eng. 116 40–5
[17] Mallakpour S, Abdolmaleki A and Moosavi S E 2015 Green route for the synthesis of ZnO by PVA/Oly(Vinyl alcohol) as a biocompatible coupling agent Polym. Plast. Technol. Eng. 54 1448–56
[18] Alder C M, Hayler J D, Henderson R K, Redman A M, Shukla L, Shuster L E and Sneddon H F 2016 Updating and further expanding GSK’s solvent sustainability guide Green Chem. 18 3879–90
[19] Liu B, You Y, Zhang H, Wu H, Jin Y and Liu H 2016 Synthesis of ZnO nano-powders via a novel PVA-assisted freeze-drying process RSC Adv. 6 110349–55
[20] Cicilliati M A, Silva M F, Fernandes D M, de Meio M A C, Hechenleiter A A W and Pineda E A G 2015 Fe-doped ZnO nanoparticles: synthesis by a modified sol–gel method and characterization Mater. Lett. 195 64–6
[21] Coulter J B and Birnie D P 2018 Assessing tauc plot slope quantification: ZnO thin films as a model system Phys. Status Solidi 255 1700393
[22] Maya-Treviño M L, Villanueva-Rodríguez M, Guzmán–Mar J L, Hinojosa–Reyes L and Hernández–Ramírez A 2015 Comparison of the solar photocatalytic activity of ZnO–Fe2O3 and ZnO–Fe3O4 on 2,4D degradation in a CPC reactor Photochem. Photobiol. Sci. 14 543–9
[23] Fatehah M O, Aziz H A and Stoll S 2014 Stability of ZnO nanoparticles in solution. Influence of pH, dissolution, aggregation and disaggregation effects J. Colloid Sci. Biotechnol. 3 75–84
[24] Sigolo F A, Davolos M R and Jafelici M 1997 Morphological evolution of zinc oxide originating from zinc hydroxide carbonate J. Alloys Compd. 262–263 252–3
[25] Znaidi L, Soler Illia G J A A, Benyahia S, Sanchez C and Kanaev A V 2003 Oriented ZnO thin films synthesis by sol–gel process for laser application Thin Solid Films 285 357–62
[26] Anžlovar A, Kogež K, Črničak Orel Z and Žigon M 2011 Polypol mediated nano size zinc oxide and nanocomposites with poly(methyl methacrylate) by electrospinning Polym. Lett. 5 604–19
[27] Abebe B and Ananda Murthy H C 2018 Synthesis and characterization of Ti–Fe oxide nanomaterials for lead removal J. Nanomater. 2018 1–10
[28] Penn R J 1998 Imperfect oriented attachment: dislocation generation in defect-free nanocrystals Science (80-. ). 281 969–71
[29] Zhang I, Huang F and Lin Z 2010 Progress of nanocrystalline growth kinetics based on oriented attachment Nanoscale 2 18–34
[30] Muñoz–Rojas D, Oró–Solé J and Gómez–Romero P 2008 From nanosnakes to nanosheets: a matrix-mediated shape evolution J. Phys. Chem. C 112 20312–8
[31] Liu X, Ye L, Liu S, Li Y and J X 2016 Photocatalytic reduction of CO2 by ZnO micro/nanomaterials with different morphologies and ratios of (001) facets Sci. Rep. 6 38474
[32] Chen M, Zhao Z, Yan Q, Hu Z, Xiao X and Chen D 2016 The effect of crystal face of Fe3O4 on the electrochemical performance for lithium-ion batteries Sci. Rep. 6 29381
[33] Zhao J, Zhao Z, Li N, Nan J, Yu R and Du J 2018 Visible-light-driven photocatalytic degradation of ciprofloxacin by a ternary MnO2/Mn3O4/MnO4 valence state heterojunction Chem. Eng. J. 353 805–13
[34] ALothman Z 2012 A review: fundamental aspects of silicate mesoporous materials (Imaterials (Basel). 5 2874–902
[35] Thommes M, Kaneko K, Neimark A V, Olivier J P, Rodríguez-Reinoso F, Rouquerol J and Sing K S W 2018 Physiosorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report) Pure Appl. Chem. 87 1051–69
[36] Zhao X S, Lu G Q (M) and Millar G J 1996 Advances in mesoporous molecular sieve MCM-41 Ind. Eng. Chem. Res. 35 2075–90
[37] Liu I, He J, Wang L, Li R, Chen P, Rao X, Deng L, Rong L and Lei J 2016 NiO–PTA supported on ZIF-8 as a highly effective catalyst for hydrocracking of Jatropha oil Sci. Rep. 6 23667
[38] Cohen E R, Mills I, Strauss H L, Frey J G, Mills I, Homann K and Kuchitsu K 2007 Quantities, units and symbols in physical chemistry Int. Union Pure Appl. Chem. 233 11–3

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[41] Cohen E R, Mills I, Strauss H L, Frey J G, Mills I, Homann K and Kuchitsu K 2007 Quantities, Units and Symbols in Physical Chemistry (RSC Publ.)
[42] Raghupathi K R, Koodali R T and Manna A C 2011 Size-dependent bacterial growth inhibition and mechanism of antibacterial activity of zinc oxide nanoparticles Langmuir 27 4020–8
[43] Santhoshkumar J, Kumar S V and Rajeshkumar S 2017 Synthesis of zinc oxide nanoparticles using plant leaf extract against urinary tract infection pathogen Resour. Technol. 3 459–65
[44] Das B, Dash S K, Mandal D, Ghosh T, Chattopadhyay S, Tripathy S, Das S, Dey S K, Das D and Roy S 2017 Green synthesized silver nanoparticles destroy multidrug resistant bacteria via reactive oxygen species mediated membrane damage Arab. J. Chem. 10 862–76