Progress of zinc oxide-based nanocomposites in the textile industry

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Abstract
Textile materials have been enriched in function at the composite level with continuous developments in the textile industry. Zinc oxide (ZnO) nanoparticles (ZnO-NPs) are strongly influenced by ultraviolet (UV) filter, antifungal, high catalysis, and semiconductor/piezoelectric coupling characteristics. Therefore, the antibacterial property and UV resistance of ZnO-NP materials are comprehensively analysed to provide a basis for applying ZnO-NP in the textile industry. In addition, the textile preparation and application of ZnO-NP in piezoelectric power generation is discussed. Based on relevant documents for ZnO-textile industry applications, scanning electron microscopy analysis, biological activity analysis, and UV transmittance analysis of textiles containing composite materials prove that textiles based on ZnO-based composite materials (ZnO-NP materials) have antibacterial properties and UV resistance. The antibacterial property and UV resistance of ZnO-NP materials are analysed comprehensively to provide a basis for applying ZnO-NP in the textile industry. After the photocatalytic reaction, its practical application as slurry type suspensions is limited because of the difficulty of separating the catalyst particles. In terms of its piezoelectric power generation characteristics, intensity of current voltage analysis and X-ray diffraction analysis reveal that textiles based on ZnO-NP materials have obvious semiconductor characteristic and obvious current enhancement signals locally, indicating that the textiles can achieve better piezoelectric properties.

1 | INTRODUCTION

With continuous developments in science and technology, people have also increasingly demanded new requirements for products and services provided by different industries while accepting the convenience brought by technology. In the fields of petrochemicals, pesticides, and organic chemicals, emerging technologies improve the purification rates of chemical products. In addition, the technology of constructing new materials based on nanomaterials is changing the fields of chemical, biological, and organic materials [1]. The improved materials have the performance that conventional materials do not have, improving the application value of products in different industries [2]. The textile industry is selected as an example. Textiles can shield and protect the body and also help cover people, prevent ultraviolet (UV) rays, and avoid harmful substances from entering the human body. The preparation of functional nanotextile materials can give textiles new functions, enhancing their application value [3].

ZnO has many excellent properties, including thermal stability, chemical stability, and electromechanical coupling. Research based on ZnO is becoming popular with its continuous discovery of potential applications. ZnO is a type of direct wideband gap optoelectronic semiconductor material [4]. Its crystal structure and lattice constant are similar to those of gallium nitride (GaN). It has many excellent characteristics in the applications of electronic and optoelectronic devices. The material is transparent to visible light and the wavelength is in the near-UV region. Its exciton binding energy index is significantly higher than room temperature thermal ionisation energy (26 meV), and excitons after composition can keep stable at room temperature. ZnO also has radiation resistance, biocompatibility, and thermal stability. It can be used to construct alloy systems with adjustable band gaps. Moreover, it
is easier to obtain raw materials. Nanoprocessing gives it some special properties that general \( \text{ZnO} \) products do not have in terms of light, electricity, magnetism, and heat, including a series of chemical and physical properties.

The crystal structure of \( \text{ZnO} \) is the space group of the hexagonal system \( P_{\text{hex}} \); the coordination number of both \( \text{O}^{2-} \) and \( \text{Zn}^{2+} \) is 4, belonging to the fibrous zinc ore structure. The tetrahedral structure of \( \text{ZnO} \) leads to its non-centrosymmetric properties, which directly leads to its pyroelectric and piezoelectric effects. At room temperature, the band gap of \( \text{ZnO} \) is about 3.2 eV and the exciton beam energy can reach 60 meV. \( \text{ZnO-NP} \) reduces the particle size of \( \text{ZnO} \) to nanoscale. The miniaturisation of the particle size has led to a sharp increase in its specific surface area, causing \( \text{ZnO} \) materials to produce macroscopic quantum tunnelling effects [5], surface effects [6], and small size effects [7]. In the textile industry, the cloth that people wear will be immersed in UV, X-ray, infrared, and visible light. Excessive UV rays can damage the human immune system and accelerate skin ageing. Because of the quantum size effect of \( \text{ZnO} \), the band gap of \( \text{ZnO} \) will exceed 4.5 eV if the particle is set to 10 nm [8], so it can absorb UV rays well. Moreover, \( \text{ZnO-NP} \) activates oxygen in the air by absorbing energy and promotes the reaction of oxygen ions with organics, inhibiting or killing a lot of bacteria and viruses. \( \text{ZnO} \) has piezoelectricity; a nanogenerator based on \( \text{ZnO} \) was first developed by Wang Zhonglin. This feature can be used in textiles to make clothes that people wear sensitive and conductive to positioning and searching during movement.

### 1.1 Application of nanomaterials in textile industry

The continuous development of nanotechnology has promoted its further expansion in the field of textile dyeing and finishing, resulting in good application prospects. The current textile field includes the following applications:

1. Nanofibre [9], which is a nanoscale linear material that can achieve some functions that ordinary fibre cannot;
2. Nanopowder [10], which refers to solid powder particles with a diameter of less than 100 nm; functional nanopowder can be dispersed in the fibre for spinning, obtaining functional fibres; or it can be dispersed in a solution to prepare fabrics to give them new functions.
3. Nanoemulsion [11]: the active emulsion ingredient in the nanosolution is at the nanolevel, which can improve the efficacy of the finishing agent.
4. Nanointerface materials, which establish nanophase regions with different properties on the macrointerface of the material, including the formation of nanoscale uneven structures on the surface of the fibre, obtaining interface nanomaterials different from the physical and chemical structure of the fibril surface.

Research on nanotechnology in the textile industry is mainly focussed on preparing high value-added and multifunctional composite fibres [12]. It is anti-UV, antistatic, antibacterial, deodorising, antimicrowave, far-infrared, and water and oil proofing, so it can effectively improve fabric performance. Among them, some nanoparticles (NPs) (\( \text{TiO}_2 \) and \( \text{ZnO} \)) have excellent light absorption properties. Adding them to synthetic fibres can absorb a large amount of UV rays. Clothing and supplies made of this fibre material can avoid UV radiation damage. For example, Matsushita prepared an anti-UV fabric material that reflects UV rays and converts the energy absorbed by UV rays into heat energy to be released [13]. Some metal particles (such as nanocopper and nanosilver) have bactericidal properties. Compounding of chemical fibres can prepare functional fibres with strong antibacterial properties, because the specific surface effect and interface volume effect of some nanoscale metals or metal oxides promotes the enhancement of the chemical activity of composite spinning, showing strong antibacterial properties [14]. Electromagnetic wave radiation comes from home appliances, communication equipment, electronic products, and radar systems. This type of magnetic waves can seriously threaten human health. Because of the small size effect and large specific surface area of NPs, they have greater electromagnetic wave transmittance and can absorb electromagnetic waves better in contrast to ordinary materials.

Chemical fibre products made of natural fibres can absorb dust owing to electrostatic friction and discharge energy characteristics, which cause a lot of inconvenience to users. Nanotechnology provides a solution to the electrostatic problem of chemical fibre textiles, which refers to compounding NPs to chemical fibre products to produce a good electrostatic shielding effect [15, 16] and suppressing the electrostatic effect. For example, wool fibre has a higher equilibrium moisture regain, but its mass specific resistance is higher in natural fibres, which easily accumulates charges. If NPs are compounded on wool fibre products, the electrostatic effect will be greatly reduced. Applying nano-ceramic powder and adhesive with a far-infrared function to the surface of pure cotton, polyester cotton and other fabrics forms a strong nano-far infrared fabric with good water resistance and antibacterial properties; it also absorbs the energy of the human body and surroundings. Pretreatment of different textiles with super-double phobic technology can give it an isolation function to isolate water stains and oil stains [17–19]. Polyvinyl alcohol is used as a raw material in some research to prepare nanofibres with a superhydrophobic surface. They are rearranged on the surface of the nanostructure due to the reduced, showing superhydrophobicity.

### 1.2 Crystal structures of \( \text{ZnO} \)

There are three crystal structures for \( \text{ZnO} \) [20]: are rock salt, sphalerite, and wurtzite. Under natural conditions, the thermodynamically stable phase of \( \text{ZnO} \) is a hexagonal fibre mineral structure corresponding to each crystal structure [21–23]. The morphology of \( \text{ZnO} \) crystals changes with changes in environmental conditions. When the pressure increases at room temperature and the value reaches 9 GPa,
ZnO crystals change from a hexagonal wurtzite structure to a tetragonal rock salt structure, which is similar to the structure of sodium chloride (NaCl) crystal. The neighbouring atoms of the crystal will increase from four to six in the new structure and the volume is reduced to 80% of the original owing to the reduction of the layer. After the pressure gradually drops, the crystal gradually has a metastable state. However, the structure still maintains the tetragonal rock salt structure [24]. It is assumed that the current ZnO crystal structure exhibits a zinc blended structure, so it has to grow on a cubic structure substrate to ensure stability. Some researchers used the first principles to obtain the energy of three different crystal structures of ZnO: −5.638 eV (wurtzite structure), −5.586 eV (sphalerite structure), and −5.478 eV (rock salt structure), as shown in Figure 1.

The wurtzite structure is taken as an example here. Its crystal structure with special properties is shown in Figure 2. The corresponding space group of the crystal structure is C6v4, lattice constant $a = 0.32485$ nm, $c = 0.5322$ nm, and the calculation of close-packed structure parameters shows that the index is ideal.

The rest of the work is organised as follows. Section 2 provides an overview of the preparation method of ZnO NP-based material. A detailed study of ZnO NP-based textiles and the results are discussed in Section 3. Finally, concluding remarks are provided in Section 4.

## 2 | PREPARATION METHOD OF ZnO NANOPARTICLES-BASED MATERIAL

As a photocatalyst, nano-ZnO is non-toxic, harmless, and stable in performance and structure. In the field of photocatalysis, air or oxygen can be used as an oxidant for a green and environmentally friendly catalyst with strong application prospects. Various methods have been applied to obtain ZnO powder with a small particle size, sparse distribution, and good performance, including physical and chemical methods. The chemical method is a relatively common nanoscale split synthesis method that features a relatively simple implementing device, low cost, and easily achieved large-scale production. The preparation method of the split body is summarised as shown in Table 1.

### 2.1 | Various morphologies of ZnO

Because of the special crystal structure, ZnO can spontaneously organise its crystal plane for growth and can grow in different directions. Adjusting different growth methods and growth conditions (such as reaction solution concentration and growth time) can promote ZnO to achieve rapid control in different growth directions, obtaining ZnO with different morphologies [36, 37]. In the morphological structure of ZnO, there are many micronano-type structures (linear, rod, and scaly). A flowchart is shown in Figure 3.

Different styles and rich shapes of nanostructures are divided into different dimensions, including 0-dimensional, one-dimensional, and multidimensional nanostructures [38, 39]. The one-dimensional structure is selected as an example here. The ZnO under this structure is linear, so the particle size in the three-dimensional space is nanometre-scale with different lengths, and the material appears as a hollow structure or a sparse structure. Because of the small size effect and quantum tunnelling effect of nanomaterials, ZnO prepared in nanometre size exhibits new characteristics in optical, electrical, mechanical, and other properties [40–42].
3 | RESULTS AND DISCUSSION

This section details the properties of ZnO NP-based textiles, the UV resistance of ZnO NP-based textiles, and piezoelectric power generation of ZnO NP-based textiles. The effect of varying the pH and time is also obtained, analysed and discussed in this section with proper graphical representation for better visualisation and analysis.

3.1 | Study of antibacterial property of ZnO nanoparticle-based textile

As mentioned earlier, ZnO has antibacterial properties, so applying it in the textile industry can improve the performance of textiles and promote human health, as shown in Figure 4.

The development of inorganic antibacterial agents is relatively simple and become popular in research. Current inorganic antibacterial agents include silver-based antibacterial materials, metal ion antibacterial materials, and active oxide antibacterial materials. Active oxide antibacterial materials have good biocompatibility and are safety and long-lasting. Among them, ZnO is representative of such materials; it can be antibacterial by means of photocatalysis and active oxygen, as shown in Figure 5. When the energy of the photon exceeds the energy of the band gap of ZnO, electrons in the valence band can transition to the conduction band, generating highly active photogenerated holes ($h^+$) and photogenerated electrons ($e^-$). Among them, $h^+$ is oxidising. Under the combined action of air and water, $h^+$ distributed on the surface of ZnO can adsorb hydroxyl and water, which can generate hydroxyl radicals.

ZnO can slowly release Zn$^{2+}$ in the water medium. Carboxyl anions on the surface of the bacteria are negatively charged. Zn$^{2+}$ is adsorbed to the surface of the bacteria owing to its Coulomb force, which damages the cell wall, as shown in Figure 4. It can penetrate the cell membrane and soak into the inside of the bacteria, reacting with the active protein and –SH and –NH₂ in the core, so that the protein is denatured and the cell synthetase activity is reduced. As shown in the figure, the surface of the denatured bacteria turns from green to blue, which means it is partial inactivated.

The application research of ZnO-NPs for antibacterial uses is further intensified. ZnO-NPs can be compounded to polypropylene to study the influence of the light time and coupling agent on antibacterial performance. Better antibacterial properties can be produced under light conditions, and the addition of coupling agents can further enhance its antibacterial properties. The morphology/antibacterial performance correlation analysis of ZnO-NPs, ordinary ZnO, and tetrapod ZnO found that ZnO materials can generate H₂O₂ under required conditions; four-needle ZnO generates the most H₂O₂; and the antibacterial properties of different types of ZnO materials are proportional to the generated H₂O₂.

3.2 | Study of UV resistance of ZnO nanoparticle-based textile

ZnO is a kind of metal oxide particle. Its NPs have the characteristics of a small size, large specific surface area, and good refractive index. Fabrics based on a ZnO finish have good UV resistance. The composite of ZnO and other materials can further enhance its UV resistance. Some studies have adopted the dipping-drying-baking method to finish ZnO on the surface of cotton fabric to test its UV resistance, as shown in Figures 6 and 7.

Figures 6 and 7 illustrates that the ultraviolet protection factor (UPF) parameter index of cotton fabric has been

| Table 1 | Preparation method of split body |
|---------------------------------|---------------------------------|
| Method                          | Materials and devices          | Strengths                           | Weaknesses                                  | Reference |
| Direct precipitation            | Ammonium carbonate [(NH₄)₂CO₃], ammonium hydroxide (NH₄H₂O), etc | High purity, simple operation, and equipment | Poor dispersibility, wide particle size distribution | [25, 26] |
| Homogeneous precipitation       | Hexamethylenetetramine [(CH₂)₆N₄], urea [CO(NH₂)₂] | Sediment particles are uniform and dense, and easy to realise | Reaction process takes a long time and reaction temperature is too high | [27] |
| Solid phase method              | ZnSO₄·7H₂O and anhydrous Na₂CO₃ | Reaction conditions are relatively mild, and output efficiency is high | It is difficult to grind sufficiently | [28, 29] |
| Spray pyrolysis                 | Aqueous solution of zinc acetate dihydrate | Good dispersibility, small particles and high purity | More energy consumption and high cost | [30] |
| Laser-induced chemical vapour deposition | Continuous wave carbon monoxide (CWCO) laser, inert gas, and zinc salt | High-energy conversion efficiency and consistent size | It had a low yield and high cost | [31, 32] |
| Sol-gel method                  | ZnCl₂, Zn(NO₃)₂, Zn(CH₃COO)₂, and ZnSO₄ | Low required temperature, high product purity | Washing and filtering are complicated | [33] |
| Microemulsion method            | Zinc salt emulsion             | It is easy to operate and particles are uniform and controllable | Material cost is high | [34, 35] |
greatly improved after ZnO is added. Comparisons on UVA and UVB show obvious decline trends after the ZnO is added, which means that the transmittance of UV rays of different wavelengths has dropped significantly. In Figure 8, the UPF of the fabric exceeds 50 under the sol-gel method. After repeated washing, the UPF of the fabric can still maintain a high value, indicating that the material stability of the fabric is significantly improved. The sol forming a film on the fabric can significantly reduce the UV transmittance of the fabric, reducing the UVC transmittance to 2%.

In Figure 7, silk fabric has different transmission effects on different wavelengths of UV light. When the wavelength is 280–300 nm, the transmittance of UV light is low, and then it suddenly rises and stays above 30%. The reason is that when the wavelength is 276–290 nm, the absorption characteristics of the fabric material and the tyrosine and tryptophan in silk protein are similar. They will react photochemically with UV rays, absorb UV rays, and reduce the damage of UV rays to skin. The main chain peptide bond of the silk protein molecule is broken, the molecular chain is cleaved, and the silk becomes yellow and discoloured, affecting the performance of the fabric. In the wavelength range of 300–400 nm, the UV transmittance of different fabric samples is significantly reduced after the fabric is finished with nano-ZnO, because UV light will adsorb nano-ZnO.
particles is less than 100 nm, the band gap will increase to 4.5 eV, which can absorb UV light with a wavelength of 280–400 nm.

3.3 Study of piezoelectric power generation of ZnO nanoparticle-based textiles

Nanogenerators can convert mechanical energy (bending of the body, swinging of the arms, flow of air, etc.) into electrical energy under different environments. Based on this mechanism, a type of self-powered nanopower generation device is prepared. The device can collect mechanical energy and generate electricity, so it has been widely used in many fields. In terms of sensors, changes in electricity can be positioned and pressure tested. Nanopowered devices can be used on insoles to achieve power generation during walking.

As early as 2008, Professor Wang Zhonglin led the team to grow ZnO nanowires on Kevlar fibres, making the nanogenerators flexible. The entangled friction of multiple fibres can achieve piezoelectric power generation. The design idea of this nanogenerator is to plate a layer of gold film on the fibres of different growth ZnO nanowires and replace the original probe as the contact electrode. Each coated nanowire has to be paired with an untreated ZnO nanowire because the number of contact electrodes increases greatly, greatly increasing the piezoelectric charge. Lee et al. used the piezoelectric properties

**FIGURE 6** Comparison of ultraviolet (UV) resistance indexes before and after the addition of ZnO nanoparticles

**FIGURE 7** Effects of ZnO to UV resistance of textiles under sol-gel mode

**FIGURE 8** The effects on UV resistance performance of silk fabric by adding ZnO-nanoparticles (NPs) under different preprocesses. 1 indicates silk fabrics without ZnO-NP materials; 2–9 refers to silk fabrics with different ZnO-NP materials and different processes

**FIGURE 9** Piezoelectric test of a single ZnO nanorod
of ZnO to prepare a flexible nanogenerator that can maximise the output performance of the nanogenerator.

Khana et al. prepared a nanogenerator based on conductive cotton fabric and introduced electrodes on the cotton fabric using a suspension coating process; the ZnO nanorods were grown on the surface of the conductive layer. It showed that both ends of the cotton fabric are coated with a sparse white coating before growth. After the growth of ZnO nanorods, the coating surfaces become dense. The team prepared a large number of nanorods on the fabric. The piezoelectric power generation test was carried out on a single nanorod. The piezoelectric potential reached 9.85 mV using the contact mode based on atomic force microscopy, as shown in Figure 9.

Figure 9 illustrates that when the scanning probe touches the nanorods, there is no electric potential generated. When the ZnO nanorods are bent, the electric potential will increase sharply. During the contact denaturation process, the high electric potential continues to be maintained. After the nanorods are moved away, the electric potential drops rapidly. Khana et al. prepared ZnO nanorods on a new conductive fabric substrate with a hydrothermal method. Through experiments, it was found that changing the crystal particle size and specific surface area of the nanorods obtained a larger piezoelectric potential.

### 3.4 Effect of variation in pH and time

There is a significant effect on the ZnO catalyst by varying the pH reaction medium. The effect of pH is investigated for the different pH range that is, 7.0, 7.5, 8.0, 8.5, and 9.0 in the textile industry under a light source. With an increase in pH value to 8.5, the photocatalytic degradation of textile industry effluent is also increased (Table 2). The graphical representation is also shown in Figure 10 for better analysis.

There are more OH-- ions with an increase in the pH solution and more OH radicals are generated by OH-- ions by combining them with the positive holes of the semiconductor. After pH 8.5, there is a decrease in the degradation of dye. Photocatalytic degradation is affected by the time variation with dyes and pigments. The irradiation time was changed from 30 to 120 min while keeping all other factors identical, as presented in Table 3; for better visualisation, it is shown in Figure 11.

Figure 11 shows that with an increase in time to 120 min, degradation increases, and it decreases beyond 120 min.

The process of degradation of textile industry effluent is affected by the amount of semiconductor TiO₂ and ZnO powder with dyes and pigments. The catalyst concentration varies from 0.0, 0.2, 0.5, and 1.0, to 2 gm/L, as listed in Table 4 and also presented in Figure 12 for better analysis.

With an increase in the catalyst level, the degradation increases to 1.0 gm/L; after this point, degradation becomes almost constant.

This is because the number of active sites on the surface increases with the high amount of catalyst, which increases the number of •OH and O₂-- radicals. The number of substrate
molecules is insufficient above the saturation point to increase the turbidity of solution that reduces light transmission. The degradation rate is not enhanced by the further addition of catalyst and remains constant.

4 | CONCLUSION

The antibacterial property and UV resistance of ZnO-NP materials are analysed comprehensively to provide a basis for applying ZnO-NP in the textile industry. In addition, the use of ZnO-NP materials in textile preparation and application in piezoelectric power generation is analysed and overviewed. The antibacterial property and UV resistance of ZnO-NP materials are analysed comprehensively to provide a basis for applying ZnO-NP in the textile industry. In addition, its textile preparation and application in piezoelectric power generation is discussed. Based on relevant documents of ZnO-textile industry applications, scanning electron microscopy analysis, biological activity analysis, and UV transmittance analysis of textiles containing composite materials prove that textiles based on ZnO-based composite materials (ZnO-NP materials) have antibacterial properties and UV resistance. The main challenge is the modification of production methods so that they are more eco-friendly at a competitive price, by using safer dyes and chemicals and by reducing the cost of effluent treatment and disposal. To preserve the environment by reducing pollution resulting from the use of great amounts of zinc oxide, which uses an activator in rubber composite, could be a future area of concern.

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CONFlict of interest

The authors have no conflict of interest.

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