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REVIEW

Metal Oxide Nanotechnology in the Paper Industry: ZnO and TiO_2 Nanoparticles for Next-Generation Functional Papers

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The pulp and paper industries are experiencing a transformative shift due to emphasis on enhanced functional performance, desired sustainability and value-added properties. Nanotechnology offers promising opportunities to tackle the existing challenges by strategic incorporation of nanomaterials such as zinc oxide (ZnO) and titanium dioxide (TiO_2) into paper matrices as viable solutions. This review highlights the potential of these nanomaterials to convert conventional paper sheets into multifunctional smart paper with improved properties such as ultraviolet blocking, antimicrobial activity, enhanced barrier performance and increased mechanical strength. Various processing approaches for incorporating nanoparticles onto paper surfaces are illustrated, considering their environmental and economic advantages. The physico-chemical structures, characteristic properties, process of green synthesis and the interaction mechanisms of both ZnO and TiO_2 nanoparticles with cellulose fibers are elaborated. A comparative analysis of ZnO and TiO_2 NPs is presented herewith to underscore their relative effectiveness in paper-based applications. Furthermore, the existing research gaps and challenges associated with the integration of nanomaterials in the pulp and paper industry are identified. Finally, future prospects are discussed for the development of nanotechnology-enabled sustainable and high-performance paper materials. While previous reviews have discussed nanoparticle functionalised paper systems broadly, a focused consolidation of ZnO and TiO_2 based approach remains limited. The present review provides an updated overview of ZnO and TiO_2 nanoparticle-enabled paper systems highlighting recent advances in green synthesis, nanocomposite integration and multifunctional paper design. It also emphasizes the relationship between material properties, functional performance and processing considerations while providing insight into current progress and future opportunities in sustainable paper technologies.

Keywords: Paper functionalisation, Green synthesis, ZnO nanoparticles, TiO_2 nanoparticles, Smart paper, Cellulose fibers.

INTRODUCTION

Nanotechnology has been the main focus area when technological advancements are assessed and has prolonged attention as well as future scope in science and innovation [1]. The global challenges faced by pulp and paper industry are environmental sustainability, high levels of water and energy consumption, waste management concerns and the pollution problems. The industry consumes large amount of natural resources like wood, water and energy, which results in the deforestation and high carbon emissions. In the present scenario, the rationale for nanotechnology adoption in pulp and paper industry is being widely used to improve the strength, printability and barrier properties of paper [2]. The remarkable properties like surface-to-volume ratio, tunable optical properties, enhanced mechanical strength and increased reactivity of nanomaterials have paved the way for novel applications. Over the last few decades, extensive research has significantly expanded the scope of nanomaterials but at the same time it has also addressed challenges related to their synthesis, characterisation and large-scale applications.

Zinc oxide (ZnO) and titanium dioxide (TiO_2) nanomaterials have been used in pulp and paper industry to increase the functionalities of paper by enhancing antimicrobial

activity, optical properties, whiteness, brightness and for enhancing strength. They are industrially relevant and have good scalability since they are cheap, safe, widely available and easy to manufacture in bulk and provide multiple functions at a time. The demand of paper is increasing rapidly in packaging sector mainly due to the rapid growth of e-commerce, ready-to-eat foods and consumer goods. Paper has emerged as a preferred alternative to plastic, offering a more environmentally sustainable option. The nano-engineered papers can achieve similar properties of plastics making them an appropriate alternative candidate of packaging [3]. Scope of the present review article is to examine the role of nanotechnology in bringing revolution to the paper industry. The focus is upon recent developments highlighting the emerging applications of nanotechnology in paper industry.

Fig. 1 illustrates the growing demand of paper globally. Rising from approximately $7000 in 2020 to around $16,000 in 2025, each year demonstrates consistent growth with values rising exponentially from the year 2020 to 2025. This trend reflects an increasing demand and the market size for sustainable, paper-based packaging materials. The major driving factors seem to be the rapidly expanding e-commerce platforms, growing environmental concerns in view of the recalcitrant plastic waste and the global shift towards eco-friendly, biodegradable packaging solutions.

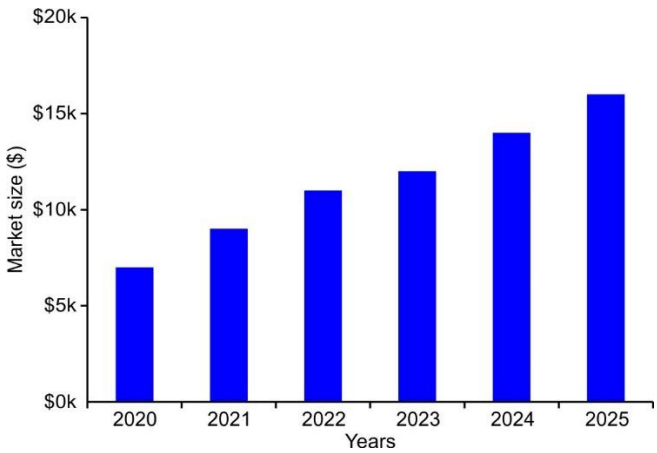

Fig. 1. Demand of packaging paper in market in last five years

Methodology: An orderly literature survey was conducted to find relevant studies related to metal oxide nanotechnology in the paper industry *viz*. ZnO and TiO_2 nanoparticles for next-generation functional papers. Multiple scientific articles, journals and databases were searched to ensure comprehensive coverage of the available research. Initially, articles were collected from four major academic sources *viz*. Web of Science, Scopus, Sciencedirect and ResearchGate. In total, 649 articles were identified during initial search process. During the screening stage, duplicate articles (334) appeared across multiple databases were removed to avoid repetition. Additionally, retracted articles (4) were excluded to maintain the reliability and scientific integrity of the review. After this process, 311 unique articles were left for further evaluation.

The literature search was conducted using a combination of structured keywords applied consistently across all selected databases. The primary search terms included "ZnO nanoparticles (NPs) functionalised paper", "TiO_2 nanoparticles (NPs) functionalised paper", "metal oxide paper functionalisation", "antimicrobial coating", "UV-blocking paper", "nanoparticle embedded paper" and "nanomaterials modified cellulose paper". These keywords were used individually and in combination using Boolean operators (AND/OR) to ensure comprehensive coverage of relevant studies.

The inclusion criteria were defined as follows: (i) peer-reviewed journal articles published between 2015 and 2025; (ii) articles written in English; (iii) studies directly reporting the application of ZnO or TiO_2 nanoparticles in paper or cellulose-based systems; and (iv) studies providing quantitative or qualitative evaluation of at least one functional property of paper, such as mechanical strength, UV-blocking ability, antimicrobial activity or barrier performance. The exclusion criteria included: (i) conference proceedings and abstracts lacking full peer review; (ii) studies focused solely on nanoparticle synthesis without application in paper or cellulose matrices; (iii) retracted articles and grey literature; and (iv) review articles that did not present primary experimental data relevant to functional paper systems.

In the preliminary screening stage, the titles and abstracts of the selected papers were carefully examined to determine relevance to the topic. In this stage, 211 articles were excluded since they contain information which was not directly related to the topic. The journal articles and reports from last 5 years containing the information related to the topic were selected. A final refinement was carried out to target 85 high quality journal articles that cover the desired information. These articles were analysed in detail to understand the synthesis, functionalisation, mechanisms and application of nanoparticle-mediated cellulose-based materials in environmental remediation and sustainable technologies. Fig. 2 depicts the selection process of reviewing the extensive literature available in the specific area of interest.

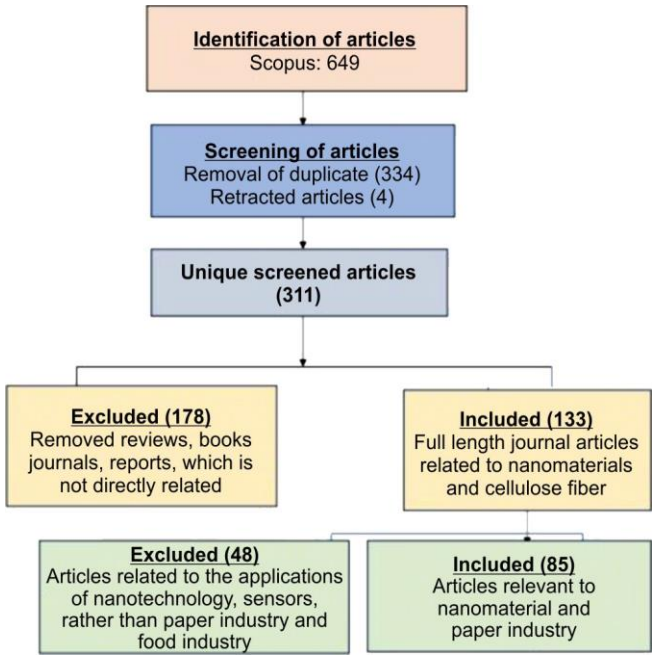

Fig. 2. Flow chart depicting the process of reviewing the literature (metal oxide nanoparticles)

Overview of nanotechnology in pulp and paper industry

Nanomaterials used in pulping processing: Nanomaterials are used in pulp processing to enhance efficiency and sustainability. They are basically used to reduce chemical consumption, reduce energy requirements and to reduce the formation of toxic effluents in pulping process cellulose fiber is separated from wood by removing lignin, hemicelluloses and other undesired components. Nanomaterials help in obtaining cellulose fiber from wood more efficiently as they are small in size, have high surface area and strong surface reactivity. Upon penetration into the cell wall, these agents become associated with lignin and hemicelluloses, leading to faster and more selective reactions. Their presence promotes the degradation of lignin and/or hemicelluloses through oxidation or hydrolysis during the pulping process. In addition, their role as enzymatic carriers contributes to a greener, more economical, and sustainable pulping process. Nanomaterials are used in pulping process to enhance efficiency, environmental benefits, to save energy and to produce better pulp quality [4]. Nanomaterials make chemical and enzymatic reactions more powerful and make pulp processing cleaner, greener as well as faster. The nanomaterials like cellulose nanofibers (CNF), nano-silica (SiO_2), ZnO nanoparticles, TiO_2 nanoparticles, *etc*. are some of the widely used nanoparticles in paper industries.

Nanomaterials used in paper functionalisation: Nanomaterials are used in paper functionalisation as they modify ordinary paper into smart paper, which have additional properties like UV-blocking, antimicrobial activity, acting as barrier as well as for strength reinforcement. Nanomaterial in cellulose fiber modifies the simple paper into high performance multifunctional material by enhancing its surface and internal structure at nanoscale level. Nanocellulose is one of the most widely used nanomaterials owing to its ability to enhance the tensile strength, stiffness and folding endurance of paper, while also improving barrier properties, surface smoothness and printability. When hydroxyl (-OH) groups in cellulose fiber interacts with paper fibers, a hydrogen bonding is formed between them thereby filling the pores to create a denser network. Another most important nanomaterials used are metal oxide nanoparticles (ZnO, TiO_2, SiO_2 and Al_2O_3). Zinc oxide are basically used to functionalize paper by enhancing antimicrobial and antifungal activity, UV-blocking and photoprotection, improving mechanical properties. Titanium dioxide is used to enhance brightness, whiteness and opacity, to improve antibacterial surfaces and photocatalytic properties. Whereas many other nanomaterials like SiO_2 and Al_2O_3 improve paper quality by enhancing its thermal stability and by increasing its water and gas barrier properties [5].

Processing routes of nanomaterials in paper: The processing route for nanomaterials in paper functionalisation refers to the manner in which nanomaterials are integrated into the cellulose fiber matrix to obtain the desired surface and functional properties. It represents the controlled approach used for incorporating nanomaterials into paper. The different methods employed for this purpose are described below and illustrated in Fig. 3.

Wet-end addition: This is the most common method used for the suspension of nanomaterials into paper. In this method, nanomaterials are added to the pulp slurry in the form of a well-dispersed aqueous suspension due to their low consistency. During integration, nanomaterials combine with cellulose fiber forming a hydrogen bonding, electrostatic attraction and mechanical entrapment as hydroxyl groups present between fibers. This method enhances paper functionalisation by improving tensile strength, stiffness, antimicrobial activity and UV-resistance. The wet-end method is mainly used for internal modification of paper instead of surface treatment, making it suitable for reinforced packaging papers and antimicrobial paper products [6].

Surface coating: It is the most effective processing route for the functionalisation of paper by incorporating nanomaterials. In this method, nanomaterials are applied on the surfaces instead of mixing them into pulp slurry. A coating of nanomaterials is applied on paper sheets by dispersing the nanomaterials in water or solvents along with binders like polyvinyl alcohol (PVA), chitosan, latex, *etc*. The binders in nanomaterial suspension help nanomaterials to bind on paper surface to functionalize paper for different applications. Such coating is applied by using different techniques like blade coating, rod coating, spray coating and dip coating [7].

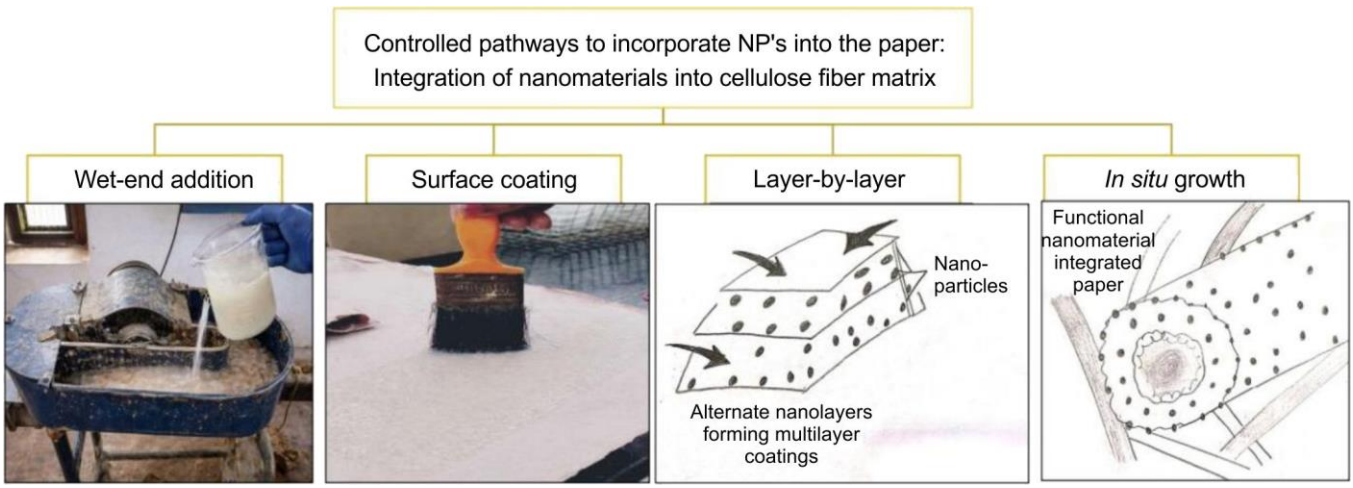

Fig. 3. Processing routes of integrating nanoparticles into paper

Layer-by-layer: In this method, a coating is developed on the paper surface through the sequential deposition of thin layers, leading to the formation of multilayer structures composed of positively and negatively charged nanomaterials. Initially, the paper surface is prepared to attract charged species. Upon immersion of the paper sheet in the solution, alternating adsorption of oppositely charged materials takes place, resulting in the formation of highly ordered multilayer nanostructures. The process resembles the stacking of ultrathin layers of different functional materials on the paper surface to enhance properties such as antibacterial activity, gas barrier performance, electrical conductivity, *etc*. [8].

***In situ* growth:** This method involves the production of nanomaterials directly on paper fibers rather than producing manually. The paper is dipped into a solution containing metal ions. These ions enter the pores and get attached to cellulose fiber followed by a chemical reaction which converts metal ions into solid nanoparticles. This process facilitates the direct generation of nanomaterials on the fiber surfaces at the desired locations. This method results into a better durability as compared to surface coating or wet-end coatings [9].

Structure-property-performance relationship: While previous reviews have addressed nanoparticle-functionalised paper systems in a broader context or considered multiple metal oxides, a dedicated consolidation of ZnO- and TiO_2 NPs based methods in relation to recent developments remains limited. Existing studies often emphasize general material classes or immobilisation strategies without specifically focusing on the evolving role of these two metal oxides in functional paper applications.

The present review provides an updated critical overview of paper systems containing ZnO and TiO_2 nanoparticles and discusses their role in the development of functional and sustainable paper applications. The review covers developments reported during the past decade, including green synthesis methods, incorporation of nanocomposites and the design of multifunctional paper systems. It also discusses the influence of material properties on paper performance and the processing aspects important for practical applications.

Zinc oxide (ZnO) nanoparticles

Physico-chemical properties relevant to paper applications: The physico-chemical properties are the properties which determine the performance of nanomaterials in paper applications at the nanoscale level. Nanomaterials have a very high surface area to volume ratio, which increases their reactivity and interaction with cellulose fibers. This results in strong interactions with cellulose fiber through hydrogen bonding, electrostatic attraction and van der Waals forces [10]. This interaction results in formation of inter-fiber bonding and enhanced mechanical properties. Another important properties include surface chemistry and surface charge which are carried by aqueous systems that helps them disperse uniformly [11]. The charged surfaces of ZnO nanoparticles and cellulose promote electrostatic interactions between them. Hydrophobicity is another important factor, as nanomaterials can create micro- and nanostructured surfaces and modify paper roughness, thereby improving water resistance. Depending on the application, such modifications may also impart optical properties, electrical conductivity, thermal and chemical stability, and antimicrobial activity. ZnO nanoparticles provide abundant active sites for adsorption, catalytic reaction and biological interactions, due to high specific surfaces area. ZnO nanoparticles have a wide direct band gap of about 3.37 eV and high excitation binding energy, which results in strong UV absorption. These combined physico-chemical properties of ZnO nanoparticle are highly suitable for applications in antibacterial agents, sensors, cosmetics and environmental remediation [12,13]. Fig. 4 is the schematic diagram of ZnO structure (4a) and (4b) is the conceptual diagram of the top surface of the ZnO/ trimethylsilyl cellulose (TMSC)-coated paper.

The interaction of ZnO nanparticles and trimethylsilyl cellulose (TMSC) is crucial in determining the way functionalised paper reacts with the biological systems. The interaction between the ZnO nanoparticles and trimethylsilyl cellulose coating mainly occurs between cellulose fibers which contain hydroxyl (-OH) group on its surface. During the coating process these hydroxyl groups are chemically modified by reacting with trimethylsilyl groups to form TMSC. Such surface modifica-

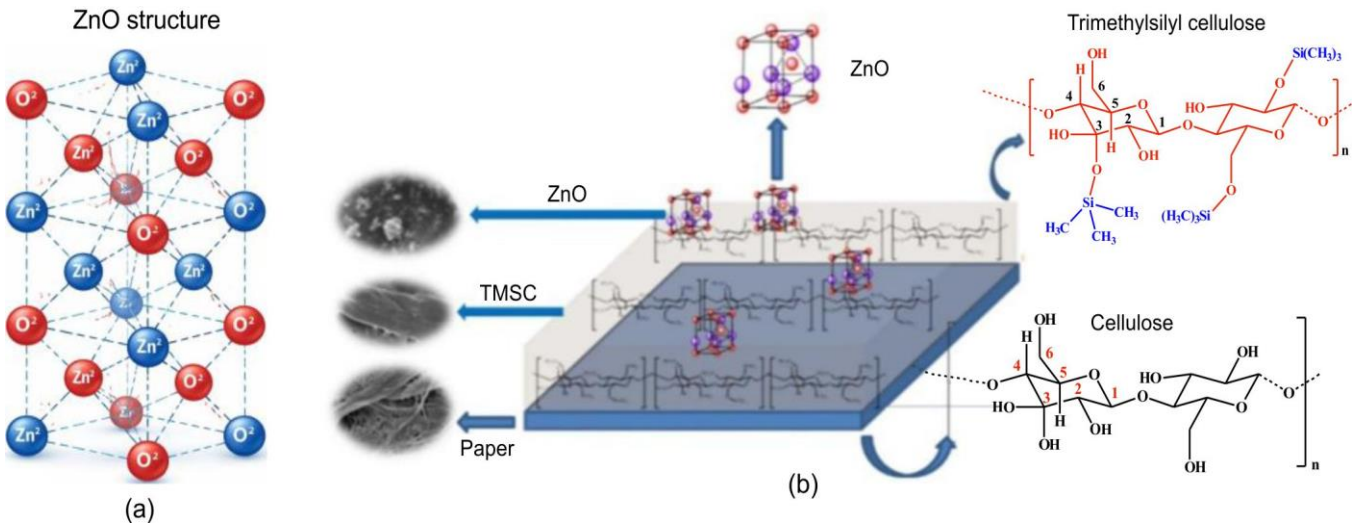

Fig. 4. (a) Schematic diagram of ZnO structure and (b) Conceptual diagram of the top surface of the ZnO/TMSC-coated paper

tions increase the hydrophobicity and reduce the polarity of the cellulose. Chemical interactions also contribute to the properties of functionalised papers. Upon contact with the coated surface, microorganisms undergo a series of biochemical reactions that can inhibit growth and cause cell death. Among these, the generation of reactive oxygen species (ROS) is considered an important mechanism, as it damages cellular components, disrupts membrane integrity and increases membrane permeability.

Green synthesis approach and sustainability aspects: Green synthesis approach of ZnO nanoparticles refers to the biological and eco-friendly methods for production of nanoparticles which are natural, non-toxic and renewable materials. Green synthesis of nanoparticles involves different approaches like plant-meditated synthesis, microbial synthesis, biopolymer assisted synthesis, *etc*. These natural sources contain bioactive compounds like polyphenols, flavonoids, alkaloids, proteins and sugars, which convert zinc salts into ZnO nanoparticles [14]. Green synthesis is a sustainable approach that reduces chemical waste, uses renewable resources and produces eco-friendly ZnO nanoparticles suitable for food and environmental applications.

Mechanism pathways with cellulose fibers: Interaction of ZnO nanoparticles with cellulose fibers occurs through electrostatic attraction, hydrogen bonding and physical anchoring. Cellulose contains hydroxyl (-OH) groups that make the fiber surface highly reactive, while ZnO nanoparticles possess hydroxylated or positively charged surface that interact with cellulose. Their nanoscale size allows penetration into fibrillar networks and inter-fiber spaces. This leads to uniform dispersion and mechanical interlocking. These interactions improve nanoparticle retention, fiber bonding, mechanical strength, antimicrobial activity, UV resistance and durability of cellulose-based paper materials [15-17]. Fig. 5 shows the interaction mechanism of ZnO nanoparticles with cellulose fiber.

Functional roles of ZnO nanoparticles in pulp and paper industry: ZnO nanoparticles are widely used in the pulp and paper industry due to their optical, antimicrobial, and surface modification properties. Their addition to paper provides antibacterial and antifungal activity, making it suitable for packaging and medical applications. Some of the important implementation of ZnO nanoparticles in pulp and paper industry are:

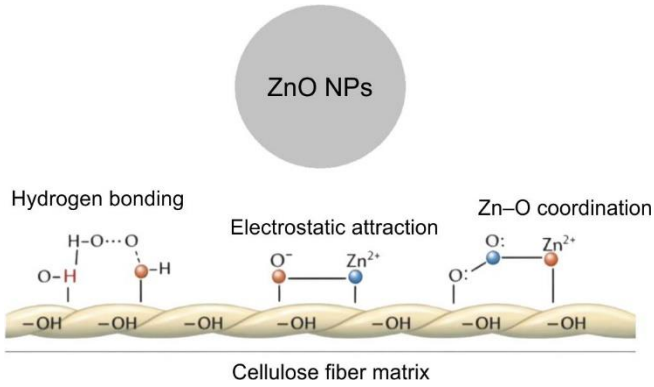

Fig. 5. Interaction mechanism of ZnO nanoparticle with cellulose fiber

Antimicrobial activity: Antimicrobial activity is the ability of substances to inhibit or kill microorganisms such as bacteria, fungi and viruses. Antimicrobial papers are produced by incorporating ZnO, Ag or plant-based agents into pulp or coatings for applications in food packaging, healthcare, hygiene and contamination detection. ZnO nanoparticles provide long-lasting antimicrobial effects through ROS generation, Zn ion release and membrane disruption [18,19]. They are also effective against multidrug-resistant (MDR) bacteria by damaging cellular proteins, DNA and lipids [20]. Recent studies focus on synergistic combinations such as ZnO NPs with antimicrobial peptides, antibiotics, plant extracts or essential oils to enhance antimicrobial efficiency [21,22]. Table-1 shows a comparative analysis of antimicrobial performance of ZnO nanoparticles.

UV-blocking and photo-protection: When ZnO nanoparticles are incorporated into cellulose, they exhibit a UV-blocking property due to their strong absorption in the UV-A and UV-B regions. Since ZnO is a wide band-gap semiconductor with a band-gap energy of E_g = 3.3 eV due to which harmful ultraviolet radiations are absorbed effectively. When UV-blocking strikes the surface of ZnO-cellulose composite, it absorbs the high-energy UV photons and electrons are excited from the valence band to the conduction band. The absorbed UV energy is subsequently dissipated as heat or harmless lower-energy radiation. This process is known as the band-gap absorption mechanism and is associated with the low refractive index of the material [27]. Cellulose contains hydroxyl groups, which interact with ZnO nanoparticles through hydrogen bonding and intramolecular interactions.

TABLE-1
COMPARATIVE ANALYSIS OF ANTIMICROBIAL PERFORMANCE OF ZnO NANOPARTICLES

Particle size and morphology	Microorganism test	Zone of inhibition (mm)	Key observations	Ref.
~20 nm, spherical ZnO nanoparticles	*Escherichia coli* and *Staphylococcus aureus*	15-26	Smaller Particles normally have a larger surface area to volume ratio which gives a more efficient mean for antibacterial activity.	[23]
~30-50 nm, hexagonal nanoparticles	*Escherichia coli* and *Pseudomonas aeruginosa*	15-22	Antibacterial activity increases as more ROS is produced in smaller ZnO nanoparticles.	[24]
~45 nm, rod-shaped ZnO nanoparticles.	*Bacillus subtilis* and *Staphylococcus aureus*	14-20	Small ZnO nanoparticles causes more membrane disruption and produce higher oxidative stress	[25]
~25 nm, spherical nanoparticles	*Salmonella typhi* and *Escherichia coli*	16-23	Increased ROS formation and membrane permeability disruption were identified as the major antibacterial mechanisms.	[26]

Such interactions improve nanoparticle dispersion and interfacial adhesion which results in interfaces between ZnO and cellulose where UV radiation is repeatedly absorbed and scattered. Since nanoparticles possess very small particle size and high surface area, the incoming UV radiations scatter effectively and provide better transparency. This scattering increases the optical path of UV rays and reduces their transmission through the material [28].

Hydrophobic and barrier properties: Hydrophobic and barrier properties is one of the most important applications of ZnO nanoparticles in the pulp and paper industry. Normal paper is hydrophilic due to the hydroxyl groups in cellulose, which absorbs water quickly. When ZnO nanoparticles are introduced into the fiber matrix or coated on the paper surface, they decrease the surface energy and develop rough nanotextured layer that helps in enhancing water repellency. ZnO nanoparticles enhance barrier properties by lowering the permeability of gases as well as migration of oils, grease and other contaminants. By providing hydrophobic and barrier properties, normal paper can be used as a smart paper for packaging and other hygiene products [29]. The latest development involves the ZnO-stearic acid-saline coatings. These combinations achieve super hydrophobicity with water contact angles up to 154º. Such type of coating maintains water repellency even after mechanical abrasion, UV exposure, *etc*. One of the other latest developments involve the CMC/ZnO blend. In this, CMC combined with ZnO nanoparticle applied *via* dip-coating improves paper density [30]. ZnO nanoparticles are increasingly integrated with cellulose derivatives and biopolymers to create super-hydrophobic, mechanically robust and antimicrobial coatings for paper and packaging applications [31].

Strength enhancement: Improvement in strength is one of the main benefits of incorporating ZnO nanoparticles into paper. Since the mechanical properties of paper largely depend on bonding between cellulose fibers, weak inter-fiber interactions can limit its strength. When ZnO nanoparticles are added to pulp or applied as coatings, they interact with hydroxyl group present in cellulose creating additional bonding sites and improving fiber-to-fiber adhesion. This results in increase of tensile strength, burst strength, stiffness and durability of the paper. In ZnO nanoparticles, a strong bonding between zinc and oxygen atoms along with their well-organised crystal structure makes the nanoparticles highly stable and resistant to damage or deformation. These properties help the material withstand external forces more effectively [32]. As a result, ZnO nanoparticles enhance the strength, stiffness, durability and crack resistance of nanocomposites and other advanced materials, making them more reliable for engineering and industrial applications [33]. Published studies have shown that ZnO nanoparticles can noticeably improve the mechanical performance of nanocomposites, with tensile strength increasing by nearly 18-45% and Young's modulus improvement by around 20-60% in various systems [34,35]. ZnO nanoparticles interact with cellulose fibers through hydrogen bonding and van der Waals force which improve fiber reinforcement and network integrity [36].

Titanium dioxide (TiO_2) nanoparticles

Physico-chemical and optical properties: TiO_2 nanoparticles possess various physico-chemical and optical properties, which make them highly valuable in packaging and paper functionalisation. Their physico-chemical properties include solubility in concentrated sulphuric acid and hydrochloric acid and insolubility in water and organic solvents, with strong ultraviolet absorption, they also exhibit high photocatalytic potential [37]. Whereas optical properties exhibit refractive index among white pigments and due to its high refractive index, it has the highest light scattering power [38]. The absorption characteristics of TiO_2 make it ideal for sunscreens and UV-protective coatings [39].

Green synthesis and crystal phases (anatase and rutile): In this approach, natural compounds present in plant extracts like flavonoids, sugars, organic acids, cellulose, chitosan, act as stabilizing and capping agents. Titanium precursors are converted to nanoparticles under mild temperature and pH conditions [40]. When titanium precursors are added to plant extract, it undergoes a hydrolysis to form Ti-OH species which then combined form Ti-OH-Ti networks. Compared to chemically synthesised TiO_2, green synthesised TiO_2 show reduced toxicity, better biocompatibility, improved dispersion [41]. TiO_2 nanoparticles have three crystalline phases *viz*., anatase, rutile and brookite. Anatase TiO_2 is widely used in papermaking due to its ability to improve brightness and whiteness, whereas rutile provides higher opacity, better UV resistance and greater chemical stability [42,43]. Anatase also possesses higher photocatalytic activity, which may lead to cellulose degradation and yellowing during long-term use if the particles are not surface treated. In contrast, rutile is generally preferred for papers intended for outdoor or long-service applications owing to its superior durability [44,45]. Although brookite exhibits interesting photocatalytic properties, its application in papermaking remains limited due to its difficulties in synthesis and lower stability [44]. Different properties of these three crystalline phases are given in Table-2.

TABLE-2
PROPERTIES OF ANATASE *vs*. RUTILE *vs*. BROOKITE TiO_2

Properties	Anatase	Rutile	Brookite	Ref.
Crystal system	Tetragonal	Tetragonal	Orthorhombic	[46]
Lattice structure	More open and less compact	More compact and dense	Less compact then rutile but more densely packed than anatase	[47]
Thermodynamic stability	Metastable	Most stable phase	Metastable	[48]
Charge carrier mobility	Moderate	Higher	Lower	[49]
Chemical reactivity	High	Lower, more inert	Moderate	[50]
Hydrophobicity under UV	Strong	Lowest	Moderate	[51]
Photocatalytic activity	Very high	Moderate to low	Moderate to high	[52]

Mechanism pathways with cellulose fiber: Interaction of TiO_2 nanoparticles with cellulose fibers mainly occurs through hydrogen bonding, electrostatic interactions and van der Waals forces. Cellulose fibers contain hydroxyl (-OH) groups that make their surface chemically active, while TiO_2 nanoparticles develop hydroxylated surfaces in aqueous media, increasing their affinity for cellulose. These interactions promote uniform attachment of nanoparticles to the fiber network rather than leaving them suspended in water. The distribution of nanoparticles during papermaking is also influenced by surface charge and pH. Uniform incorporation of TiO_2 nanoparticles improves paper properties and enhances stability within the cellulose matrix [53-55].

Functional roles of TiO_2 nanoparticles in pulp and paper industry: TiO_2 is widely used in the pulp and paper industry due to its high refractive index, strong light-scattering ability chemical stability and non-toxic nature. Its use as an inorganic filler and pigment improves the brightness, opacity, durability and inclusive performance of paper products. A detailed explanation of its applications is given below herewith:

Enhancing whiteness and brightness: In paper industry, optical appearance is characterised by whiteness and brightness. Whiteness refers to the uniform reflection of visible light by paper, resulting in a clean and neutral appearance, whereas brightness indicates the amount of blue light reflected from the paper surface [56]. It is typically measured near 457 nm and is directly associated with print clarity and image sharpness. TiO_2 is effective in improving both of these optical properties due to its high refractive index (~ 2.7), with strong intrinsic opacity. By integration of TiO_2 into fibrous matrix or by coating its layer on the paper, diffusion of light is increased on the paper surface by restricting the light transmission through the cellulose fiber network [44,45]. The incorporation of TiO_2 into paper improves surface smoothness and printability by increasing ink–substrate contrast, resulting in sharper and more distinct printed text and images. These improvements, together with enhanced optical properties, make TiO_2 an important functional pigment in the manufacture of high-quality paper products [57].

Increasing opacity: TiO_2 is widely used in the paper industry to improve paper opacity, reducing the visibility of text and images on the reverse side of the sheet [58,59]. Maximum opacity is achieved when the particle size approaches the wavelength of visible light, a phenomenon known as Mie scattering. The high refractive index of TiO_2 promotes efficient light scattering within the fiber network, particularly when nanoparticles occupy void spaces between cellulose fibers. This gives paper a more solid appearance and improves readability [60]. Such properties make TiO_2 an important pigment for printing and writing papers, magazines, newspapers, packaging materials and specialty paper products.

UV blocking photoprotection: The incorporation of TiO_2 nanoparticles into cellulose exhibit UV-blocking properties mainly strongly in UV-B and part of UV-A region. The UV radiations are absorbed by band-gap absorption mechanism in which electrons absorb the photon energy. When electrons move from valence band to the conduction band, they form electron-hole pair mechanism in which the energy gets stored since the photon energy is consumed in exciting the electron [61]. Sometimes the electron-hole pair migrate to nanoparticle surface and results in ROS generation. As TiO_2 has a very high refractive index compared to cellulose, the incoming radiation undergoes repeated internal reflection within the composite structure. When UV rays passes through TiO_2-cellulose composite, thousands of nanoparticles are dispersed throughout the material and UV-rays continuously collide with these particles resulting in an increased optical path length of light and have higher probability of being absorbed [62].

Reinforcing paper strength: TiO_2 also contributes to the enhancement of the tensile strength of paper sheets. When TiO_2 particles are dispersed within the pulp suspension, they occupy inter-fiber micro-voids and contribute to the formation of a more compact and structurally denser fiber-filler composite [63]. This interaction reduces stress concentration sites and improves load transfer within the sheet, leading to increases in tensile strength, burst resistance and folding endurance [64]. Furthermore, the surface chemistry of TiO_2 promotes interfacial interactions with cellulose through hydrogen bonding and physico-chemical adhesion, which improves fiber-fiber contact efficiency and reinforces bonding at fiber junctions. TiO_2 nanoparticles have also demonstrated considerable improvements in tensile strength, typically in the range of 10-38%, along with better hardness and elastic modulus [64]. These enhancements are mainly attributed to strong bonding between the nanoparticles and the material matrix, efficient transfer of applied stress and the ability of nanoparticles to hinder crack formation and propagation, resulting in stronger and more durable materials. This dual functionality renders TiO_2 particularly advantageous for specialty grades, packaging substrates and premium printing papers, where a combination of superior visual appearance and mechanical durability is essential for end-use performance [65].

Comparative analysis of ZnO and TiO_2 nanoparticle applications: ZnO and TiO_2 nanoparticles have attracted considerable interest in the pulp and paper industry due to their ability to improve the functional properties of paper when incorporated into the cellulose fiber matrix. Although both materials possess similar band-gap energies, their behaviour in paper systems differs considerably. ZnO nanoparticles exhibit high surface reactivity and interact strongly with cellulose through hydrogen bonding and electrostatic interactions, promoting fiber-fiber bonding and improving the mechanical strength of paper even at low loadings [17]. In contrast, TiO_2 nanoparticles are comparatively inert and contribute mainly to improved surface smoothness, opacity and coating quality rather than direct reinforcement of the fiber network [44]. The incorporation of these nanomaterials can also enhance the barrier properties of paper, making it suitable for packaging and medical applications. Table-3 presents a comparison of the characteristics and applications of ZnO and TiO_2 nanoparticles in the pulp and paper industry.

Environmental and economic advantages: The relatively low cost and multifunctional nature of ZnO and TiO_2 nanopowders have attracted considerable interest in paper-based applications. Their incorporation into the cellulose fiber network can impart antimicrobial activity, UV shielding and

TABLE-3
COMPARISON OF ZnO AND TiO_2 NANOPARTICLE PROPERTIES IN THE CONTEXT OF PAPER AND PULP INDUSTRIAL APPLICATIONS

Property	ZnO nanoparticles	TiO_2 nanoparticles	Ref.
Band-gap energy	~3.2-3.37 eV	~3.0-3.2 eV	[66]
Optical transparency	High transparency in visible region	Very high transparency and UV blocking ability	[67]
UV absorption	Strong UV-A and UV-B absorption	Excellent UV absorption, especially UV-A	[68]
Tensile strength	~20-45% increase	~15-35% increase	[69]
Antimicrobial efficiency against bacteria	~85-99% inhibition	~70-95% inhibition	[70]
Surface area activity	High surface reactivity	Stable but comparatively less reactive	[71]

improved mechanical strength, extending the use of paper in food packaging and healthcare products where protection against microorganisms and light exposure is important. Improved strength allows the production of lighter paper materials without compromising performance, reducing raw material usage and transportation costs. In certain applications, nanomaterial-assisted processing can lower the demand for chemicals and energy while maintaining product quality. The use of paper products with improved durability, recyclability and biodegradability supports the transition towards a more sustainable and resource-efficient pulp and paper industry.

Research gaps and challenges in pulp and paper industry: The pulp and paper industry consume large amounts of forest resources, water and energy causing environmental issues such as deforestation, pollution and carbon emissions [72]. To reduce these impacts, industries are adopting sustainable methods including water recycling and renewable energy use. Incorporation of ZnO and TiO_2 nanoparticles improves paper properties like antimicrobial activity, UV protection, strength and brightness. However, large-scale applications face challenges such as nanoparticle agglomeration, poor dispersion and low retention in the paper matrix due to their high surface energy and very small size [73].

Despite the promising functional properties demonstrated at the laboratory scale, several challenges must be addressed for industrial implementation of ZnO and TiO_2 nanoparticle-functionalised paper. One of the key challenges is nanoparticle retention efficiency during wet-end processing, where significant material loss can occur due to the nanoscale size and high dispersion stability of particles [74]. Strategies such as surface modification, use of cationic retention helps and optimisation of electrostatic interactions are being explored to improve nanoparticle fixation within the cellulose matrix.

The scalability of processing techniques also plays a critical role. While wet-end addition is easily adaptable to existing papermaking processes, it often suffers from lower retention efficiency. In contrast, surface coating and layer-by-layer assembly provides better control over functional properties but it may introduce additional processing steps and costs at industrial scale. From an economic perspective, the cost of nanoparticle synthesis, functionalisation and integration remains a limiting factor, particularly for large-scale production. Despite their advantages, green synthesis methods require further improvement in terms of scalability and consistency. For food packaging applications, issues related to nanoparticle leaching, environmental impact and regulatory compliance remain important considerations. The development of stable, non-leaching nanocomposite systems is necessary for the wider industrial adoption of nanotechnology-based paper products.

Surface charge influences the retention and fixation of nanoparticles in the cellulose fiber network. Since cellulose and ZnO/TiO_2 nanoparticles often carry negative or weak surface charges, their interaction and retention may be limited. Economic feasibility remains a challenge due to the cost of nanoparticle synthesis, specialised equipment and surface modification processes. Environmental concerns arise when nanoparticles are released through industrial wastewater and enter aquatic ecosystems, where they may interact with microorganisms or accumulate in the food chain, leading to the oxidative stress and cellular damage in aquatic organisms [75,76].

Future prospects of nanotechnology in pulp and paper industry: Future developments in the paper industry are directed towards improving product performance while reducing resource consumption and environmental impact. Nanotechnology offers opportunities to enhance paper strength, smoothness, durability and functional properties. Recent developments include the use of cellulose nanofibrils (CNF), cellulose nanocrystals (CNC), and bacterial nanocellulose (BNC). The role of ZnO and TiO_2 nanoparticles in these developments is shown in Fig. 6.

Fig. 6. Impact of metal oxide nanoparticles in pulp and paper industry

Developments involved in paper industry

Enhancement of recycled paper by integration of nanocellulose: Nanocellulose has attracted considerable attention in the paper industry due to its ability to improve the strength, durability and functionality of paper while maintaining low weight and biodegradability [77]. The abundance of hydroxyl (-OH) groups on nanocellulose promotes strong hydrogen bonding with cellulose fibers, enhancing inter-fiber bonding and strengthening the paper structure. The resulting three-dimensional nanofiber network fills void spaces within the sheet and improves the integrity of the fiber matrix. Such reinforcement is especially valuable in recycled papers and can reduce the need for virgin fibers, lowering raw material consumption and production costs. This effect is particularly important in recycled papers, where repeated recycling shortens fibers and reduces their natural bonding ability, leading to lower strength and stiffness [78,79].

Improvised barrier properties for food packaging: Barrier properties are important in paper-based packaging as they protect food from moisture, oxygen, grease, oil, gases, odours and microbial contamination. The porous nature of paper allows air and water vapour to pass through the fiber network, which can adversely affect food quality and reduce shelf life. Moisture can alter texture and quality, while oxygen exposure can promote oxidation and spoilage of food products [80].

Barrier performance can be improved by incorporating nanosized fillers into polymer, biopolymer or cellulose-based matrices. These nanocomposite structures increase the diffusion path for gases and liquids, forcing them to travel through a longer and more tortuous route rather than moving directly through the paper sheet. This reduces the permeability of the material to moisture and gases and improves its protective function [81]. Furthermore, nano-engineered coatings provide another route for enhancing barrier properties. Such coatings are prepared by dispersing nanoparticles in aqueous solutions of polymers such as starch or chitosan and subsequently applying the suspension onto the paper surface. The coating penetrates the fiber network, fills void spaces and reduces sheet porosity, thereby limiting the passage of air, water vapour, oil and grease [82]. When combined with ZnO or TiO_2 nanoparticles, such coatings can provide antimicrobial activity and UV protection along with improved barrier performance, making these materials attractive for food packaging applications.

Enzyme-nanomaterial synergy for pulp processing: Enzyme–nanomaterial synergy refers to the combined use of enzymes and nanomaterials to improve the efficiency and sustainability of pulping and bleaching processes. Conventional papermaking relies on chemicals for the removal of lignin, hemicellulose and residual ink from fibers during pulping and recycling operations [83]. Enzymes, being biological catalysts, selectively break down these components by targeting specific chemical bonds, thereby reducing the need for harsh chemical treatments [84].

The incorporation of nanomaterials can enhance enzyme performance by improving their stability and activity. Immobilisation of enzymes on nanomaterial surfaces provides a large surface area for enzyme attachment and promotes better contact with pulp fibers [85]. The small size of nanomaterials facilitates their movement within the fiber network, allowing enzymes to reach lignin-rich regions and ink-contaminated areas more effectively. Strong interfacial interactions, such as hydrogen bonding and electrostatic attraction, help maintain enzyme stability during processing. The combined action of enzymes and nanomaterials enables selective removal of unwanted components while preserving fiber integrity. This approach can reduce chemical consumption and improve process efficiency, making pulping and bleaching operations cleaner and more environmentally sustainable.

Conclusion

Nanotechnology has emerged as a transformative approach in the pulp and paper industry by enabling different and multifunctional properties of paper. Strategic incorporation of ZnO and TiO_2 nanoparticles enhances antimicrobial activity, strength, barrier properties, UV protection, whiteness, brightness and opacity of paper. These enhancements make nanoparticle incorporated papers suitable for food packaging, medical packaging and smart paper applications. Future developments in paper technology are expected to involve greater use of nanocellulose and enzyme-assisted nanotechnology for improving paper strength, barrier properties and process efficiency. Such approaches offer opportunities to reduce the consumption of raw materials and chemicals while supporting more sustainable manufacturing practices. Progress in this area will depend on close interaction between academic research and industrial implementation. The present review examines paper systems based on ZnO and TiO_2 nanoparticles with particular attention to their use in functional and sustainable paper products. The relationship between material properties, processing conditions and paper performance is considered to provide a clearer understanding of the current status of the field and areas that require further investigation.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

DECLARATION OF AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used an AI-assisted tool(s) to improve the language and no data, results or scientific conclusions were generated by AI. All analyses, interpretations and conclusions are the authors' own. The authors reviewed and edited the content and take full responsibility for the published work.

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