

TiO₂-containing nanocomposite structure: Application and investigation in shoes sports medical soles in physical activities

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Abstract. Wearing the right sportswear is one of the essential points in exercising, which is mainly neglected. Sportswear should be suitable for the ambient temperature and not cause more heat or cold in the athlete's body. On the other hand, increased sweating and blood circulation during exercise should not cause fatigue or heatstroke in the athlete. Nanotechnology has grown significantly in the field of producing more efficient equipment in the field of sports. The increase in demand in sports for complete sports equipment has revealed the necessity of using the highest quality materials in this sector. In the world of championship sports, a minor change in equipment can lead to significant changes in causing failure and victory. Since the sole is the most critical part of sports shoes, with the introduction of nanotechnology and nanocomposites, it is possible to help athletes rush and increase their sense of calm and satisfaction. Using nanocomposites in the soles of shoes can improve some of their characteristics, prevent the smell and sweat of shoes, and induce water repellency in these shoes. In this research, titanium dioxide (TiO₂) nanocomposite, along with cellulose, has been used to create antibacterial and hydrophobic properties in the soles of sports shoes. The synthesized nanocomposite has been synthesized using the least amount of chemicals, which shows this method's easy and cost-effective synthesis.

Keywords: physical activities; shoe soles; sport; TiO₂ nanocomposite

1. Introduction

The most essential and first exercise step is choosing the right sportswear. The first obvious point about sportswear is its feature that increases the confidence level of athletes. There is a suitable outfit for every sport. The most significant thing about wearing sports equipment is that it improves people's performance. Sportswear manufacturers are looking for appropriate materials for specific sports (Medani *et al.* 2019, Ramteke Prashik *et al.* 2019, Bamdad *et al.* 2020, Jia *et al.* 2020, Mirjavadi Seyed *et al.* 2020, Zhou *et al.* 2020). However, proper sportswear protects the athlete's body from injury (Nam *et al.* 2017). Regular exercise is essential for physical and mental health. The clothes that are chosen can have a significant effect on the athlete's performance. In addition to helping people get in the right mindset for training in the gym, they offer other benefits (Paluska and Schwenk 2000).

Sweating and Breathing: Since the athlete sweats a lot during exercise, it is helpful to wear appropriate clothing. Using breathable fabric can absorb moisture and make the athlete feel relaxed and dry. Besides its sweat-wicking ability, the excellent fabric does not promote bacterial growth. Reduced sweat and bacterial growth mean no more smelly gym clothes (Aali Mohammadi *et al.* 2022).

The durability of clothes: There is no need to spend much money to buy good and durable sports clothes. The right sports equipment is usually very durable, can be found at most sports clothing stores, and can make the most of it while it is available (Claussen *et al.* 2022).

Environmental protection: Sportswear can also help athletes protect the environment. Sports in summer should be done with breathable clothes and shoes. This keeps the body cool and prevents the smell of sweat (Ahmad *et al.* 2023).

Comfort: One of the most critical features of wearing sportswear is its comfort. For example, wearing the wrong shoes causes blisters on the feet. When the athlete chooses comfortable clothing in fabric and softness, it allows him to focus on the sport instead of feeling uncomfortable (Cheng 2022).

Improved range of motion: For better performance, the best choice is to choose an elastic piece of clothing and shoes that allow the body to move freely (Yang *et al.* 2022).

The comfort obtained from high-quality materials specifically designed to meet the needs of the active body should not be overlooked (Alsultan Abdulmajeed 2021, Dai *et al.* 2021, Alimoradlu and Zamani 2022, Behdinin and Moradi-Dastjerdi 2022, Thakur *et al.* 2022, Zhao *et al.* 2022a). Breathable and moisture-wicking materials can make workouts durable and pleasant. Such materials protect the body from overheating and impulsive cooling, which can even be dangerous to health (Hou *et al.* 2021, Huang *et al.* 2021, Xu *et al.* 2021, Wang *et al.* 2022). The right sportswear should support the body. The wash ability of the

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textile is another thing that should be considered in advance because sportswear means that it will be washed often and regularly. Repairing and adjusting clothing while exercising can be annoying and time-consuming (Salopek Čubrčić *et al.* 2022). In order to keep the feet healthy, the most critical point is to use appropriate shoes for each activity. The pressures caused by improper sports shoes are multiplied during sports activities, while suitable sports shoes can balance the pressure on the knees and hips (Hébert-Losier and Pamment 2022).

Nevertheless, in sports activities, apart from the issue of taking care of the feet by choosing the right shoes, there is also a more critical issue, which is increasing abilities and capabilities, and the right shoes can be an essential factor in this regard (Omidi *et al.* 2013, Mousavi *et al.* 2017). Using non-standard shoes harms the nerves and psyche and the efficiency of human work (Chorny *et al.* 2021). These tiny organisms reproduce in large numbers on the legs and produce organic acids – methanethiol, isovaleric acid, and propanoic acid – as waste products (Mohammadi *et al.* 2020, Wang *et al.* 2020, 2023, Ugurlu and Ozturk 2021, Dehghanbanadaki *et al.* 2022). Although they are harmless creatures, they can leave a bad smell. While sweat does not smell, these bacterial wastes combine to create an odor. Shoes are also a good place for bacteria to grow because sweat and moisture accumulate in them and create a suitable environment for the growth of bacteria. Most insoles are the source of the foul smell of the shoes (Nemati and Naemi 2022).

Foot sweat treatment is necessary for conditions where sweating is excessive. Sweaty feet are usually standard, but excessive sweating can conduct to other health problems such as foot odor, athlete's foot, and toenail fungus. In addition, sports shoes must have a suitable and robust sole because the sole is the foundation of the shoe structure and protects the athlete's foot from damage from external factors (Arlegui *et al.* 2021). The sole is a vital and influential part of the quality and output of a shoe, which, despite its high impact, should be addressed by shoe buyers. This part is located in the lowest part of a shoe and has direct contact with the ground (West *et al.* 2019). The next and essential role of the shoe sole is to create a feeling of comfort for the soles of people's feet while walking, standing, and using shoes. Some of the comfort that the sole feels in contact with the shoe is due to the softness of the sole of the shoe and its material, and another amount of the comfort of the foot that is related to the time of walking is due to the elasticity and flexibility of the sole of the shoe. The more flexible the shoe is and the easier it is to bend, the easier it is to step on different surfaces (Cranage *et al.* 2019). The only part of the shoe can be made of different materials, which may be different from the other parts of the shoe. Even in some shoes, the sole is made independently of several different raw materials to cover more features expected from a shoe sole (Dong *et al.* 2019). Therefore, athletes should look for shoes with fabric soles with antimicrobial properties and proper ventilation. In addition to sports shoes, which are a suitable place for the growth of bacteria and the spread of foul odor, sports clothes can also be affected by the foul smell of sweat

during exercise and cause discomfort to others and the athlete himself. With the help of nanotechnology, it is possible to prevent the growth of bacteria inside shoes and even other sports clothes (Zolfagharian *et al.* 2021). Nano is one of the emerging branches of technology that researchers, technologists, and entrepreneurs have welcomed in current years due to its expansive applications in various products and industries (Miteva 2021). The growing trend of using nanomaterials and products in various fields, including agriculture, medicine, and industry, has made nanotechnology one of the pioneers of technology in the 21st century (Igiebor *et al.* 2023). One of the exciting applications of nanotechnology is sports, and the published news of the development and commercialization of products based on nanotechnology in this industry shows its potential (Čibo *et al.* 2020). Nanotechnology can have useful applications in sports and cover many sports fields, including sports textiles and clothing, sports equipment, and even medical equipment for athletes (Gharehaghaji 2019). Nanotechnology has provided new opportunities for producing innovative materials that not only meet the needs of athletes but also help them to be at the highest level of safety and comfort and provide their best performance in competitions (Temesgen *et al.* 2018). The applications of nanotechnology in sports, to produce more durable and lighter clothes or to try to eliminate the foul smell of clothes after heavy sports activities, are all in line with this innovation and creative efforts (Abbasi *et al.* 2020). Perhaps, the only difference between nano products and other types of innovation can be seen as the emerging nature of this technology compared to many fields of knowledge, through which unique properties are achieved. An odor- and sweat-proof garment that dries quickly or an ultra-light tennis racket, or even a bicycle with low weight but high strength can be cited as examples that draw the attention of sports enthusiasts to this particular technology (He *et al.* 2022). One of the biggest global problems in sports is smelly sports clothes and equipment. Sports equipment is a suitable breeding ground for the growth of bacteria and fungi that cause infection, odor, sores, itching, or foot odor (Guduru and Gupta 2022). If these bacteria and fungi are under control, it is possible to control the foul smell of clothes and infection. Fabrics and products modified with nanotechnology are used for various activities, such as ballooning, parachuting, snowboarding, aerobics, cycling, athletics, hockey, climbing, swimming, sailing, sailing, skiing, etc (Chen *et al.* 2021, Esparham *et al.* 2021, Raj *et al.* 2021, Shahram Ghaedi Faramoushjan Hossein Jalalifar 2021, Ting Cai Yousef Zandi 2021, Maheswaran *et al.* 2022, Shariq *et al.* 2022). Considering these sports' challenging conditions, using sports clothes and equipment with multi-purpose features is crucial (Darabdhara and Ahmaruzzaman 2022).

Nanocomposites include multi-phase materials in which at least one of the constituent components has a size of fewer than 100 nanometers in one dimension (Popescu *et al.* 2022). In these materials, when one of the phases reaches nano dimensions, the properties of the nanocomposite change compared to conventional composites of the same phases (Wu *et al.* 2023, Zhang *et al.* 2023, Zhao *et al.*

2023). These materials show particular and more desirable properties than conventional composites because the forces between the standard surface of the reinforcement and the background in a nanocomposite are more potent than the size of these forces in a typical composite due to the nanometer dimensions of the reinforcement particles (Hu *et al.* 2010). Nanocomposites are of two parts. The main base comprises matrix, reinforcement, polymer, metal, and ceramic (Chen *et al.* 2017, Li *et al.* 2022, Su *et al.* 2023). Each of these types of composites has different applications based on their characteristics. Polymer matrix composites are composed of a polymer resin as a matrix or filament as a reinforcing agent (Omanović-Miklićanin *et al.* 2020). Among the features of this category of composites, we can point out diverse and expansive applications, good properties at ambient temperature, ease of manufacturing, and low cost. In metal-based composites, the base has a flexible metal (Zhao *et al.* 2021, 2022b). Compared to polymer composites, the advantages of this type of composite are that it has a higher operating temperature, is non-flammable, and is more resistant to the invasion of organic fluids (Pitsa and Danikas 2011).

Titanium dioxide nanocomposite (TiO₂) has a diameter of less than 100 nm, and titanium dioxide improves impact strength, tensile strength, and softening temperature and has antibacterial properties (Zhang *et al.* 2022, Guo *et al.* 2023, Huang *et al.* 2023, Tang *et al.* 2023). This chemical composition can be used on floorboards or other types of floor coverings to increase the shine and strength of these products against wear materials (Ghosh and Das 2015).

In this work, titanium dioxide cellulose nanocomposite has been synthesized to use its antibacterial, physical, and mechanical properties in the soles and soles of sports shoes and other sports clothes and to prevent the foul smell of foot sweat from the soles of shoes. Along with the water-repellent properties of the soles of these shoes.

2. Experimental

The list of materials and tools prepared for synthesizing cellulose-TiO₂ nanocomposite to deal with bacterial factors that cause the foul smell of sweat in clothes and sports shoes and increase the strength of shoe soles is shown in Table 1.

3. Methods

3.1 Synthesis of cellulose-titanium dioxide nanocomposite

To make cellulose-titanium dioxide nanoparticle composites by controlled hydrolysis method, Titanium tetrachloride was used in the presence of cellulose fibers. For this purpose, 30 ml of TiCl₄ was added to deionized water, and the volume of the solution was brought to 500 ml. Since the resulting solution is a colloidal solution, ultrasonic waves for Solution homogenization were used. After homogenizing the solution, 7 grams of urea was added to the above mixture. The pulp sample was first

Table 1 List of materials and devices

Titanium tetrachloride (TiCl ₄)
Urea
Deionized water
Ultrasonic
Scanning electron microscope (SEM)
Field emission scanning electron microscope (FESEM)
Thermal analysis (TGA)
X-ray diffraction (XRD)
Vortex Mixer
Incubator



Fig. 1 Shoe sole containing nanocomposite (Cardoso *et al.* 2019)

dissolved in hot water in an ultrasonic bath, and the fibers were separated using a disintegrator, then, the pulp was washed with deionized water. Then 8 grams of cellulose fibers were added to the colloidal solution of titanium dioxide. The resulting solution was stirred for 3 hours in an ultrasonic bath at a temperature of 60 degrees Celsius. The cellulose fiber-titanium dioxide nanocomposite was filtered using Whatman filter paper and thoroughly washed with distilled water. This material was used in shoe soles and soles, and its antibacterial effect was investigated to control foot odor and increase the strength of shoe soles.

3.2 Measurement of antibacterial properties

In order to investigate the antibacterial property of shoe soles made from cellulose-titanium dioxide nanocomposite, the modified soles were subjected to the growth of some known pathogenic bacteria, such as *Staphylococcus aureus* and *Enterobacter aerogenes*, under standard conditions (Fig. 1). The mentioned bacteria were directly exposed to visible

Table 2 Percentage inhibition of bacteria by Cellulose-TiO₂ nanocomposite in shoe soles

Percentage Microbial reduction		Sample
Staphylococcus	Enterobacter	
0	0	Normal Shoe soles
96	99	Shoe soles+Cellulose-TiO ₂

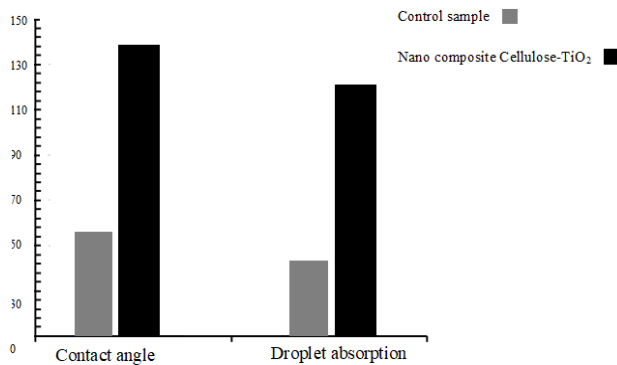


Fig. 2 The results of droplet absorption test and droplet contact angle in cellulose-titanium dioxide nanocomposite

light under favorable conditions for bacterial growth. The number of bacteria was measured before the test and 24 hours after the exposure using the American Association of Textile Chemists and Colorists - Antibacterial Finishes on Textile Materials Test Method. In this method, $1-2 \times 10^3$ CFU/ml bacteria samples were transferred separately to Petri dishes containing solid culture medium and placed in an incubator under temperature conditions of 45°C for 24 hours. Then, a portion of each sample was transferred to tubes containing 7 ml of physiological serum and vortexed. After this stage, 80 µl of the medium containing bacteria was added to the tryptic medium of the agar culture by the surface culture method and kept at 45 for 24 hours. Then the number of colonies in the plates was counted.

3.3 Measurement of physical and mechanical properties

The physical properties of shoe soles obtained from modified fibers, such as droplet contact angle and absorption, were measured. Furthermore, their tensile strength was measured by examining the resistance characteristics of modified insoles.

3.4 Investigating the structural characteristics of cellulose-TiO₂ nanocomposite

The morphological characteristics of the cellulose-TiO₂ nanocomposite, including the shape, size, and placement of nanoparticles on cellulose fibers, were investigated using a scanning electron microscope (SEM). The investigation of the surface structure of fibers has been done by a field emission scanning electron microscope (FESEM). The titanium dioxide's crystallinity phase was evaluated using X-ray diffraction (XRD). Thermal analysis (TGA) was used to measure the number of minerals in cellulose fibers.

4. Results

4.1 Antibacterial test results

The spread of various diseases caused by pathogenic bacteria and their resistance to antibiotics has forced researchers to search for hygienic and safe methods to produce suitable products for a better and healthy life for people. With the advent of nanotechnology, nanomaterials such as titanium are used as antimicrobial agents. In this method, the antimicrobial efficiency of sports shoe sole samples made with titanium dioxide-cellulose nanocomposite was investigated in reducing two common types of bacteria, *Staphylococcus aureus*, and *Enterobacter aerogenes* are the sources of various infections. Quantitative results are reported in Table 2. Standard shoe soles without this type of nanocomposite did not have antimicrobial properties. Nevertheless, in samples made with titanium dioxide-cellulose nanocomposite, the percentage of bacteria decrease is significant. This can be attributed to the increased contact between bacteria and nanocomposite, which destroys the wall membrane and bacterial enzymes.

4.2 The results of droplet absorption test and droplet contact angle in cellulose-titanium dioxide nanocomposite in shoe soles

The results of the shoe sole water absorption test are shown in Fig. 2. The results show that the contact angle of the drop on the surface of the sole made of the resulting nanocomposite has increased by about 70 degrees. The absorption of the drop in the sole of the shoes has been done at a lower speed, which means a decrease in water absorption in the modified soles. Titanium dioxide is a highly hydrophilic material, but the process conditions of making these particles are a very influential factor in changing the chemical structure of the surface of these particles and ultimately providing different behavioral characteristics of these particles. Suppose titanium dioxide particles are produced in an acidic environment. In that case, they show hydrophobic properties, and if the production environment of these particles is alkaline, it leads to the creation of hydrophilic properties in these particles. In this research, the acidic environment of urea was used to make a nanocomposite, which led to the hydrophobicity of the soles of the shoes.

Fig. 3 shows the SEM images of titanium dioxide nanocomposite and cellulose-titanium dioxide nanocomposite. In Fig. (a), the average size of TiO₂ nanoparticles is approximately 100 nm. The morphology of cellulose-TiO₂ particles is not much different from plain TiO₂ particles, and the average particle size is close to that of plain TiO₂. However, the materials of cellulose-TiO₂ particles appear with less aggregation, and the surface of cellulose-TiO₂ particles is rougher than plain TiO₂ (Fig. 3(b)).

The nanocomposite's surface structure was investigated by a field emission scanning electron microscope (Fig. 4). In the sample made with nanocomposite, the presence of TiO₂ nanoparticles on the fiber surface is straightforward

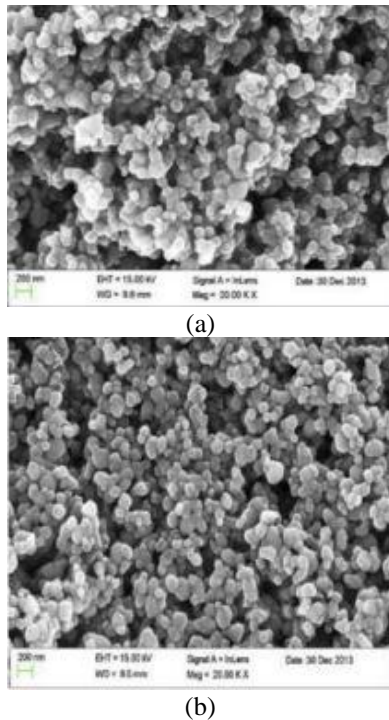


Fig. 3 SEM images for (a) TiO₂, (b) cellulose-TiO₂

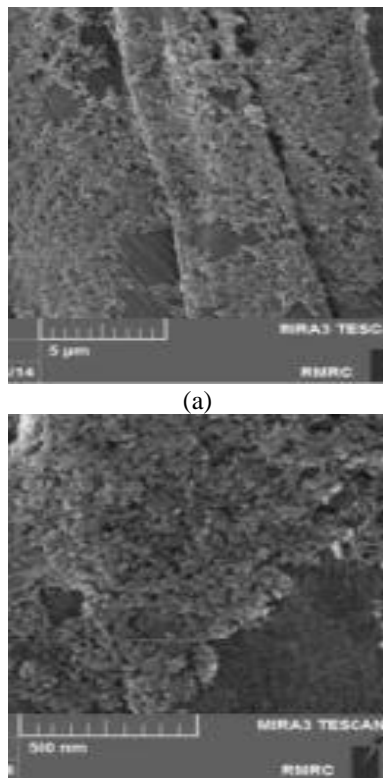


Fig. 4 FESEM images of nanocomposite, (a) sample with TiO₂, (b) Sample with cellulose-TiO₂

Table 3 The percentage of minerals in the samples

Name	The percentage of TiO ₂	Ash percentage
Cellulose-TiO ₂	13	12
Cellulose	-	0.8

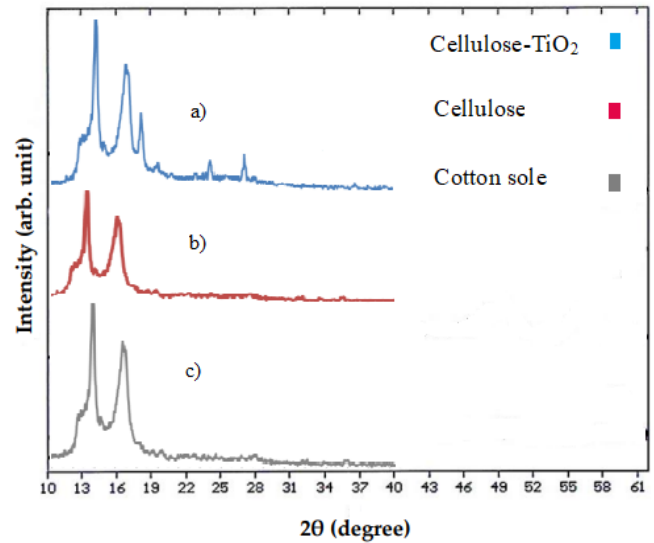


Fig. 5 XRD pattern

(Fig. 4(a)). There are ridges on the sample surface that confirm the presence of cellulose on the surface of the sole coating. Fig. 4(b) shows that the sample's surface is well covered with the nanocomposite.

4.3 XRD results

The XRD test results are shown in Fig. 5. In Fig. 5(a), the spectrum is related to the cotton sole covering with shoes- Cellulose-TiO₂ nanocomposite. In Fig. 5(b), the spectrum is related to the cotton sole covering shoes with cellulose. Furthermore, Fig. 5(c) is related to the cotton sole of shoes without additives. In the samples, the diffraction angle is observed at 14 and 20 degrees due to the presence of cellulose. In covering the samples with nanocomposite, the existing peaks indicate the phases of anatase and rutile titanium dioxide. This nanocomposite is layered with a homogeneous and uniform coating on the shoe's sole. Anatase is a metastable mineral form of TiO₂ with a tetragonal crystal structure. Furthermore, Rutile is an oxide mineral formed of TiO₂, the most common natural TiO₂.

4.4 Thermogravimetric test results

The thermogravimetric test was performed in the temperature range of 50 to 600 degrees Celsius. Fig. 6 and Table 3 show the results of this test. The results showed that the samples had a very mild weight loss of up to 370 degrees Celsius, and their weight decreased sharply with the increase in temperature. So, the amount of virgin cellulose fiber ash reached about 0.8%. In contrast, in cellulose nanocomposite-titanium nanoparticles, the results were very different, so the weight loss of these particles in the temperature range of 370 degrees Celsius started with a steep slope and reached about 35%, and with increasing temperature decreased more than the weight of the particles with a gentler slope and finally reached 12% (Table 1). The results showed the absorption of 13% by weight of titanium dioxide nanoparticles on the fiber surface.

5. Discussion

It is necessary to have suitable sports shoes for all sports activities, including running, walking, and working with equipment in the gym or various sports. Injuries caused by wearing the wrong shoes can stop fitness progress. Athletes' most common problems are sweaty feet and foot odor. Sweating in the feet is more due to wearing shoes, so attention to foot hygiene is more important than other parts. Excessive sweating can disrupt a person's regular and daily life. Problems such as bad smells, dirty clothes, and infection in the sweating area are the most common problems. The type of shoe sole is also effective in the amount of foot sweating and can reduce and improve this problem. Introducing nanotechnology into the clothing field, especially the shoe industry, has led to the development and increase of the quality of shoes. This goal is pursued by using the science of nanotechnology for the process of waterproofing shoe products and making shoes antibacterial because doing sports such as football, climbing, and other sports and physical training activities in humid environments and even on rainy days with water infiltration inside the shoes causes many problems to occur. It creates a problem for athletes. Because the foot is in the shoe for a long time, it causes sweating and the growth of microbes, creating terrible foot odor and an unpleasant feeling. Therefore, these problems can be solved with the help of nanoscience. The use of nanotechnology in textile materials, including nanofibers and nanocomposite fibers, as well as finishing textiles with nanomaterials, creates multiple properties in textiles, which makes their use attractive in the sportswear market. A nanocomposite is a composite with at least one component in dimensions between 1 and 100 nanometers. The first phase is a crystal structure, which is the base or matrix of the nanocomposite and may be made of polymer, metal, or ceramic. The second phase is nanometer-scale particles distributed within the first phase as reinforcement for specific purposes such as strength, resistance, electrical conductivity, magnetic properties, etc. Among the various properties of nanocomposites are the high surface-to-volume ratio, high flexibility without reducing strength and scratch resistance, and favorable optical properties such as transparency, which depends on the size of the particles. From the structural point of view, particles and fibers usually cause strength in the substrate. The polymer substrate can uniformly transfer the forces applied to the composite to the reinforcing material by sticking to the mineral materials. Types of nanocomposites include polymer-based nanocomposites, ceramic-based nanocomposites, and metal-based nanocomposites.

6. Conclusions

Exercising is one of the best activities that, in addition to creating a sense of vitality, also makes the athlete fit and healthy. In the meantime, wearing suitable sports clothes is one measure that makes sports activities more enjoyable. In other words, wearing the right clothes while exercising and

making the body look more beautiful also improves the body's function. Because by controlling the flow of air, it prevents excessive sweating of the body. Wearing the right shoes is one of the other things the athlete must follow to exercise. In other words, whether professional sports such as bodybuilding are done, and the daily walk is done, wearing the right sports shoes is inevitable. Because some possible injuries during exercise are related to improper foot position, it is better to prepare shoes suitable for the type and amount of activity before performing any sports activity.

In the current research, the sole of sports shoes has been modified by cellulose-titanium dioxide nanocomposite, which has performed a good activity against the odor and sweat of athletes' feet, according to the results obtained, and they also have hydrophobic properties. SEM and FESEM tests confirmed the synthesized nanocomposite's quality on the shoe sole's surface. Furthermore, spectrum XRD showed that the cellulose nanocomposite was uniformly distributed on the surface of the shoe sole. This nanocomposite improves the characteristics of the sole of the shoe in terms of antimicrobial properties to reduce foot sweat and prevent athlete's foot odor and water repellency. In order to have a quality nanocomposite with desirable characteristics, some requirements must be considered when making nanocomposites. Good dispersion and proper distribution of nanofillers in the entire polymer field is one of the essential requirements. The meaning of dispersion is to prevent clumping, and proper distribution is the proper dispersion of all particles in the field. The nanocomposite synthesized in this method has proper dispersion and distribution.

Looking at the work done in this field, it can be seen that unlike some fields of nanotechnology, such as nanomedicines, the use of nanotechnology in improving sports equipment requires less investment and less specialized equipment. The variety of applications of known nanocomposites and nanofibers in improving the properties of sports equipment is one of the advantages of this field.

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