ATATÜRK ÜNİVERSİTESİ YAYINLARI
ATATURK UNIVERSITY PUBLICATIONS

Review Article DOI: 10.5281/zenodo.14533985

Overview of radiation shielding properties of tungsten oxide nanofibers

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ABSTRACT

Nanotechnology has garnered significant attention for providing innovative solutions across various fields, including fire safety, agriculture, corrosion protection, and environmental management. In the context of fire safety, nanostructured materials play a critical role, while in agriculture, nanoagrochemicals enhance crop protection and improve productivity. Similarly, nanoparticles used in corrosion protection significantly prolong the lifespan of materials. From an environmental perspective, these nanomaterials present eco-friendly and sustainable alternatives. Additionally, tungsten oxide (WO_3) has emerged as a key material in several industrial and technological applications, including diagnostic tools, protective equipment in healthcare, photocatalysis, electrochromic devices, energy storage, and radiation protection. The research also highlights the selective cytotoxicity of tungsten oxide-based composites, such as tungsten oxide-polyvinyl alcohol (PVA), tungsten oxide-polyvinylpyrrolidone (PVP), and tungsten oxide-thermoplastic polyurethane (TPU), particularly in targeting cancer cells, along with their radioactive properties. The process through which these materials are transformed into fibers what it is also discussed in detail.

Keywords: Nanotechnology, Tungsten oxide, Composite, Radioactivity properties

INTRODUCTION

Nanotechnology has become a rapidly developing technology field in recent years due to the development of innovative solutions in various fields such as materials science, agriculture, health and environmental management. Nanotechnology has played an important role in many sectors from fire safety to agriculture, from corrosion protection to environmental applications, and nanomaterials and nanostructures obtained with Nanotechnology have shown superior performance and efficiency compared to traditional methods. However, with the development of this technology, some difficulties such as intellectual property rights and human health have been encountered. Nanotechnology is used in the development of protective equipment and materials in the field of fire safety. Nanostructured materials that are specifically developed to reduce fire risks are produced and this equipment is integrated into the materials to reduce the risk of fire [1]. Nowadays, nanoagrochemicals in agriculture offer effective solutions to protect plants against diseases, weeds and pest species [2]. In addition, the positive effects of nanomaterials on plant germination and growth have been proven by scientific studies. These innovations are not only increase agricultural productivity, but also minimize environmental impacts and contribute to sustainable are agricultural practices. According to research, WO_3 nanoparticles are known to support plant growth by increasing seed germination. However, it was concluded that WO_3 nanoparticles doped with molybdenum (Mo) supported faster and healthier growth in plants. For example, in crops such as kodo millet, this material significantly increased seed germination rate and early growth success. At the same time, WO_3 exhibited antifungal properties against plant pathogens, increasing the productivity and durability of agricultural crops. For example, its photocatalytic bactericidal properties improve the environmental quality of agricultural areas by reducing ammonia concentration and pathogenic bacteria levels [3–9]. After agriculture, applications of nanotechnology in the field of corrosion protection have also gained significant popularity. Nanoparticles and nanocoatings increase the durability and safety of the material substrate and provide superior corrosion resistance. In addition, self-healing nanocomposites are being produced. These nanocomposites repair themselves regardless of damage, extend the life of the materials and minimize maintenance costs. Thus, they both support crop production and contribute to sustainable agricultural practices. The superior hydrophilic and oleophobic properties of WO_3 are of great importance in environmental technologies, especially in the field of water treatment. For example, WO_3 -coated stainless. steel mesh and other composite membranes separate oil-water mixtures with a separation efficiency of up to 98%. In addition, these membranes break down organic pollutants under UV light, providing self-cleaning, long-term performance and sustainability. Nanomaterials developed for wastewater management and reduction of gas emissions support environmental sustainability by adding value to industrial by-products [10].

Received	19.10.2024
Revised	03.12.2024
Accepted	10.12.2024
Publication Date	20.12.2024

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Cite this article: Gücenmez E., Duras S., Koluman A. Overview of Radiation Shielding Properties of Tungsten Oxide Nanofibers. *NanoEra*. 2024;4(2):81-89

In addition, the photocatalytic activity of WO_3 plays a critical role in water treatment processes. Because its reactive oxygen species (ROS) production capacity has effectively eliminated microorganisms and pollutants, making access to clean water much easier [7,11–13]. In the field of energy storage, WO_3 offers high density and theoretical capacity. WO_3 is used as an electrode material for supercapacitors. By creating WO_3 nanostructures, we can improve its electrochemical performance and increase its energy density. For example, in symmetric supercapacitors, WO_3 has shown superior performance in terms of both energy density (34.45 Wh/kg) and power density (18.75 kW/kg). Moreover, thanks to its electrochromic properties, WO_3 has enabled the visualization of energy levels in energy storage devices through color change. This feature has provided a great advantage when used in integrated energy systems [14–20]. Nanotechnology also plays an important role in the healthcare sector. It has played a critical role in improving health security, especially during the COVID-19 pandemic. Nanoparticles are being investigated as effective carriers for vaccines, along with advanced diagnostic tools and protective equipment, and contribute to the improvement of delivery systems [21]. These innovations are of great importance for protecting and improving public health. However, despite the numerous advantages offered by this technology, it should be recognized that there are also potential risks to human health and the environment [2].

In the biomedical field, WO_3 nanoparticles show selective cytotoxicity against cancer cells while protecting healthy cells. This effect is associated with the pH sensitivity of WO_3 and its ability to generate reactive oxygen species (ROS). These properties allow WO_3 to induce apoptosis in cancer cells, making it a potential agent for targeted cancer therapies.

In human health, WO_3 attracts attention with its unique properties in cancer treatment. In fact, when WO_3 is modified with compounds such as polyglycerol and hyaluronic acid, it provides an increase in the drug carrying capacity specifically targeted to tumor cells. Therefore, WO_3 -based materials stand out as both effective and safe drug carriers [5,22–26]. For example, the ability to absorb near-infrared light makes WO_3 an ideal choice for photothermal therapy (PTT) and photodynamic therapy (PDT). In this process, WO_3, activated by laser light, destroys cancer cells through localized heat production, and this process is a highly effective method for tumor treatment. However, studies have proven that WO_3 nanoparticles have a direct cytotoxic effect on cancer cells. For example, experiments on human breast cancer cells (MCF-7) determined that 50% of the living cells were destroyed within a 24-hour period. Such success shows that WO_3 is one of the most promising materials of the future not only in cancer treatment but also in drug delivery systems. Moreover, the low cytotoxicity of WO_3 nanoparticles towards stem cells increases the safety and biocompatibility of this material [27–30]. As a result, nanotechnology offers revolutionary solutions in many sectors such as fire safety, agriculture, corrosion protection and healthcare. However, strengthening regulatory frameworks and ensuring public confidence are essential for the safe and effective implementation of this technology. This field, which is full of continuous growth and innovation, has seen extensive growth in the global market due to the versatile applications of tungsten oxide (WO_3) in sustainable and safe applications in various fields such as photocatalysis, electrochromic devices and energy storage systems. With its high stability, tunable band gap and unique electrochemical properties, WO_3 makes it a valuable component for many industries. Known for its high efficiency in photocatalytic processes such as pollutant degradation and CO_2 reduction, especially due to its band gap ranging from 2.5 to 2.7 eV, tungsten oxide offers innovative approaches to sustainable energy production through its integration with carbon-based composites [31]. This integration process enhances the optimization of photocatalytic efficiency and enables the development of promising solutions for environmentally friendly energy production. WO_3 finds wider application in WO_3 electrochromic devices, especially in smart windows and displays. Its superior electrochromic properties include high tinting efficiency and durability [32]. WO_3 is a versatile transition metal oxide that can be used in various high-tech applications such as optoelectronics, photocatalysis and sensors. The performance of this material depends on properties such as crystal structure, oxidation states and the presence of oxygen vacancies. WO_3 is an n-type semiconductor that usually exists in monoclinic and hexagonal phases, exhibiting high electrical conductivity and electron mobility. These properties make it suitable for use in gas sensors and electrochromic devices [33]. Oxygen vacancies in non-stoichiometric forms, such as WO_{3-x}, improve photocatalytic efficiency by increasing light absorption and affect the photochromic properties of the material [34]. Moreover, WO_3 thin films can be deposited by various techniques, such as thermal evaporation and chemical vapor deposition.

Their optical and electrical properties can be further improved by nanostructuring. However, there are still challenges to optimize the properties of this material, ensure its continuity in manufacturing processes, and increase stability under operational conditions.

This makes it difficult to fully realize its potential for advanced functional materials and smart devices. In recent years, developments in deposition techniques such as high-power pulsed magnetron sputtering have been optimized to improve the optical and electrochromic functions of WO_3 films [35]. These developments increase the market potential of WO_3, making it suitable for a wider range of applications [36]. The flexibility and efficiency of these devices make them suitable for a variety of applications and support innovative solutions in the field of energy storage. However, there are still several challenges in optimizing the performance and scalability of such capacitors for commercial use, requiring continuous research and development efforts [37].

The wide range of uses and unique properties of this material contribute to its increasing demand in the global market. With a wide range of applications ranging from photocatalytic processes to electrochromic devices and energy storage systems, this material is particularly in increasing demand in the global market.

GENERAL PROPERTIES OF TUNGSTEN OXIDE NANOFIBERS

The properties of WO_3 nanofibers vary depending on the synthesis methods and structural properties. For example, uniform nanofibers with a diameter range of 297–429 nm can be obtained by ultrasonic vapor deposition, while polycrystalline tungsten nanofibers with a diameter of 107 nm can be produced by needleless electrospinning technique [29]. These nanofibers are usually in monoclinic phase, which increases their surface area and light absorption capacity [38].

Black WO_{3-x} nanofibers improve their electrical conductivity and catalytic properties due to their low oxygen vacancies [38]. However, there are difficulties in large-scale production and consistent performance. Future studies should focus on optimization of synthesis processes and better understanding of the factors affecting the performance of nanofibers.

Properties of tungsten oxide and polyvinyl alcohol (PVA) nanofibers

WO_3 filled polyvinyl alcohol (PVA) composites have structural, optical and photocatalytic properties and therefore are of great interest in industries. WO_3 nanoparticles (Fig. 1) [39] are embedded into PVA nanofibers by electrospinning to obtain fibers with diameters ranging from 125 nm to 165 nm. These fibers can be obtained homogeneously by using surfactants (e.g., CTAB), thus affecting the morphology and diameter of the fibers. WO_3-PVA composites show high photocatalytic activity, especially for decolorization of methylene blue under UV (ultraviolet) light. Doping of WO_3 nanoparticles significantly enhances the photocatalytic property.

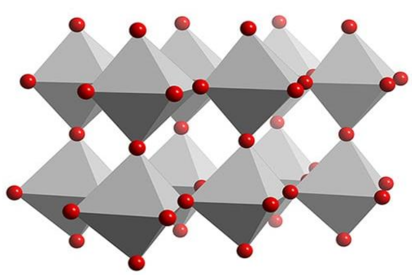


Fig. 1. 3D view of Tungsten Oxide [39]

Furthermore, WO_3 microfibers also exhibit effective photocatalytic activity in the degradation of Rhodamine B under UV light, enabling environmental remediation applications.

WO_3-PVA nanofibers are optically remarkable due to their high conductivity and low absorption properties. Nanoparticle content and electrospinning parameters affect the optical properties of these fibers, and these fibers exhibiting zero band gap energy are useful for various optical applications. Moreover, PVA deposited WO_3 thin films offer high electrochromic coloration efficiency and optical modulation, making them suitable for electrochromic devices.

The synthesis of PVA-doped WO_3 includes precipitation, coagulation and solvent casting methods. The process starts with dissolving the tungsten salt in water and mixing it with PVA. This mixture is then subjected to a heat treatment between 400-700°C. The average particle size of the obtained WO_3 is in the range of 20-50 nm. The specific surface area of the obtained product is between 10.5-21.5 m²/g. The structure obtained with this method consists of a semi-crystalline PVA matrix containing WO_3 nanoparticles.

Its chemical content is characterized by complexes formed through intermolecular hydrogen bonds between PVA and WO_3. These bonds increase the structural stability and functionality of the material. For characterization studies, the chemical and structural properties of the material are analyzed in detail using techniques such as FTIR, XRD, SEM and EDAX.

In conclusion, PVP and PVA doped WO_3 synthesis methods offer a powerful method to develop high-performance electrochemical materials. These methods provide a wide range of applications by providing both structural homogeneity and chemical stability [28,29].

Radiation protection features

WO_3-PVA composites (Fig. 2) [40] have also shown promising results in the field of radiation protection. Studies show that increasing the WO_3 concentration in PVA matrices significantly increases the gamma-ray attenuation coefficients. Nanocomposites provide superior protection compared to microcomposites due to the higher surface-to-volume ratio of WO_3 nanoparticles. Monte Carlo simulations have confirmed that nano-WO_3 outperforms micro-WO_3 fillers and that PVA/WO_3 composites provide effective protection against high-energy gamma photons [34]. These composites are lighter than traditional shielding materials and exhibit low conductivity, making them ideal for a variety of applications.

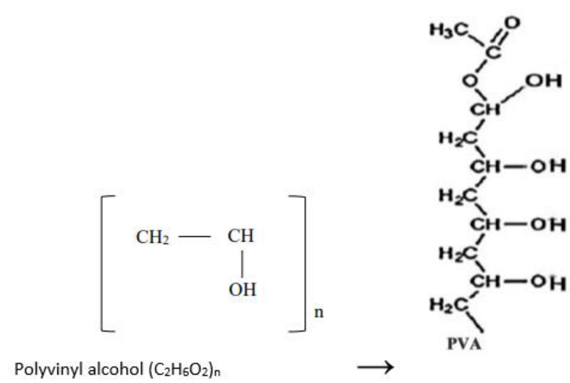


Fig. 2. Schematic view of tungsten oxide-PVA. [40]

Furthermore, WO_3-coated magnetic nanoparticles are promising for cancer treatment via neutron activation and magnetic hyperthermia (which uses the ability of magnetic nanoparticles to generate heat by vibration in an alternating magnetic field). These nanoparticles offer biocompatibility and hydrophilicity, increasing their usability in medical applications.

General properties of tungsten oxide - PVP nanofibers

Polyvinylpyrrolidone (PVP) stabilized WO_3 nanoparticles are characterized by their photochromic and photocatalytic performances. PVP enhances the stability of WO_3 while accelerating the formation of reduced tungsten species under UV irradiation, which improves their photochromic recycling ability. WO_3 nanoparticles can be effectively used in photocatalysis processes, which play an important role for environmental remediation applications.

WO_3 combined with polyvinylpyrrolidone (PVP) has also shown promising results in cancer treatment. These nanoparticles exhibit selective cytotoxic effects in cancer cells while showing minimal toxicity to healthy cells. This is due to the pH sensitivity and reactive oxygen species (ROS) generation ability of WO_3. WO_3 nanoparticles increase intracellular oxidative stress, leading to apoptosis in cancer cells.

The optical properties of WO_3 are further improved when combined with PVP. For example, PVP/WO_3 composites exhibit photochromic and photocatalytic properties as well as improved thermal stability and ionic conductivity, offering potential for use in areas such as energy storage and polymer solar cells [44].

The synthesis of PVP-doped WO_3 involves several steps based on the chemical composition and structural properties of the material. In this process, the use of dispersants such as polyvinylpyrrolidone (PVP) is important to improve the homogeneity and stability of WO3. The steps and characteristics of this method are as follows:

Dissolution and mixing

PVP is dissolved in deionized water and is usually obtained by combining with other polymers (P123). Then, hydrochloric acid (HCl) and sodium hydroxide (NaOH) are added to adjust the pH of the solution. This step ensures the stable preparation of the materials.

Precipitation

Substances such as sodium tungstate, used as a tungsten source, are added dropwise to the solution in a controlled manner. This process results in the formation of tungsten acid precipitates, which form the intermediate product required for the following steps.

Calcination

The resulting mixture is calcined at high temperatures (usually between 400-700°C) to form the desired WO_3 structure. This step improves the crystal structure and thermal stability of the material.

Doping

To improve the electrochemical properties of WO_3, it can be doped with metal ions such as zinc or yttrium. This process is an important step to improve the performance of tungsten oxide.

Use of polymeric binders

PVP plays a binding role in the WO_3 structure used as the electrode material. This improves the mechanical stability and electrochemical performance of the material.

Hydrothermal method

The hydrothermal method allows ultra-fine WO_3 particles of approximately 10 nm in size to be obtained. This nanometric size significantly improves the properties of the material such as conductivity and electrochemical activity.

Homogeneous composition and structural characterization

The balance between particle sizes and mole ratios during preparation ensures that the additives are evenly distributed within the homogeneous WO_3 matrix. This positively affects the performance of the material [41].

Tungsten oxide - PVP and radioactivity

The interactions of WO_3 nanoparticles with radioactivity have attracted interest, especially in radiation protection and therapeutic applications. WO_3 plays an important role in cancer treatment when used as a radiation dose enhancer. PVP-stabilized WO_3 nanowires have the potential to improve radiation therapy and photothermal therapies by providing heat and singlet oxygen production under NIR laser excitation. The VESPR appearance of WO_3 is as shown in the figure (Fig. 3) [42].

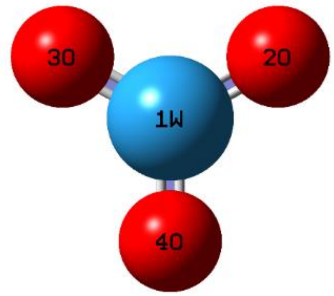


Fig. 3. VESPR view of WO_3 [42]

Tungsten oxide and TPU properties

WO_3 is a versatile and functional material with potential for use in various application areas [27]. When incorporated into polymer composites, WO_3 significantly improves the optical and mechanical properties of these materials.

For example, when WO_3 nanoparticles are used in thermoplastic polyurethane (TPU) matrices, the mechanical strength and thermal stability of the composites are also increased. Moreover, when WO_3 thin films are produced by magnetron sputtering, the optoelectronic properties can be optimized by adjusting the deposition parameters. Such thin films can be used in advanced technological applications such as transparent electronics.

Tungsten Oxide - TPU and radioactivity

Recent research has revealed the interactions of WO_3 with radioactivity and its potential in radiation shielding applications. Incorporation of WO_3 nanoparticles into polymer and cement matrices enhances the radioprotective properties of these materials [43]. The incorporation of WO_3 into glass and polyester composites leads to higher radiation attenuation capabilities, increasing their linear attenuation coefficients and effective atomic numbers [4]. Its morphological appearance is as shown in Figure 4 [44-45].

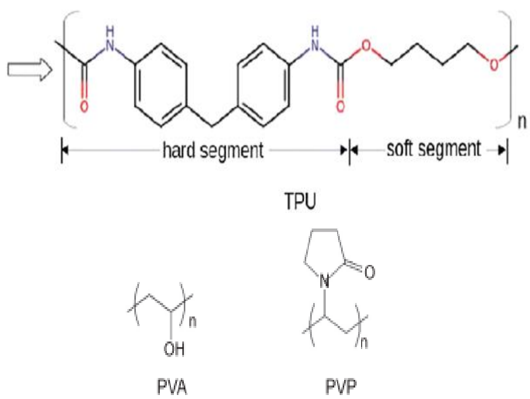


Fig. 4. Schematic view of tungsten oxide-TPU, tungsten oxide-PVA and tungsten oxide-PVP [44,45]

Combination with WO_3 PVP and PVA

The combination of WO_3 with PVP significantly increases its dispersibility in processing solvents and improves its photochromic properties, including bleaching rate. PVP acts as an effective organic ligand that optimizes the performance of tungsten oxide composites for practical applications (Figure 5.a.). The combination of WO_3 with PVP polymer stabilizes WO_3 nanoparticles and affects their structure [46]. Sodium cations significantly affect the photocatalytic behavior by promoting the formation of reduced tungsten species (W+5) upon UV irradiation and cause structural changes. It also increases the ionic mobility and reduces the optical energy gap [44]. It also highly improves the thermal stability and AC conductivity of the composite due to the interactions during complexation and charge transport. When WO_3 nanoparticles are combined with PVP polymer, the light-matter interaction is enhanced, the band gap is reduced and the localized defect states are increased. In this case, composite nanofibers improve the nonlinear absorption behavior. When WO_3 is combined with PVP polymer, tungsten undergoes thermal treatment. This treatment results in the removal of PVP and the growth of crystalline WO_3.

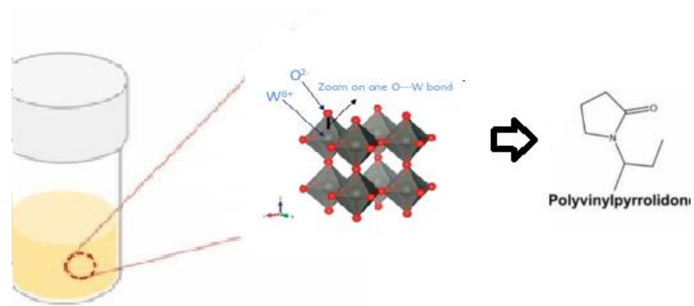
As a result of this treatment, the morphology of the nanofibers forms a rough surface and smaller diameter, improving the gas sensing properties [44].

When WO_3 is incorporated into the PVA polymer (Figure 5.b.). Interactions and complexes are formed with the OH groups of PVA. This results in structural repositioning. After this positioning, the crystallinity changes and complexes are formed, which lead to a changing structural order due to the decreased crystallinity and decreased intermolecular interactions between the PVA chains [47,48]. This causes changes in the microstructural properties and improves the mechanical properties of the composite. When WO_3 is incorporated into PVA, changes also occur in the structural, thermal and radiation protection properties of the composite [9,29]. The interaction improves dispersion, reduces crystallinity and increases mass attenuation coefficients, making the composites effective for protection against X and γ rays, resulting in more durable and improved materials. It is emphasized that the WO_{3-x}/Ag_2WO_4 photocatalyst increases photocatalytic disinfection and supports wound healing when loaded into the PVA hydrogel. When combined with PVA polymer, it facilitates better dispersion of nanoparticles and helps in obtaining thinner and straighter nanofibers during electrospinning [49]. When WO_3 is combined with PVA, flexible nanocomposites with rod-like morphology are formed.

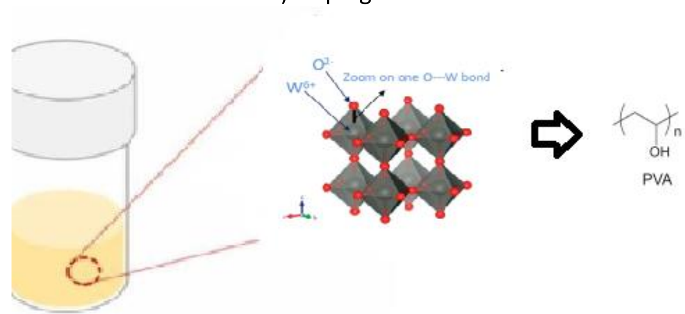
During synthesis, the formation of nano-sized particles is increased, resulting in an average size of 20-50 nm and minimal aggregation, which contributes to a high specific surface area of 10.5-21.5 m^2/g [28,36,46,50–54].

COMPARISON OF TUNGSTEN OXIDE (WO_3) AND POLYMER BASED COMPOSITES WITH ALTERNATIVE MATERIALS

In this study, alternative materials that offer similar structural, optical, photocatalytic and radiation protection properties to those offered by WO_3 and polymer-based composites were investigated. The suitability of these materials was evaluated.



a) Doping PVP



b) Doping PVA

Fig. 5. View of PVA and PVP. [18, 28]

Titanium dioxide (TiO_2)

TiO_2 is a material with high photocatalytic activity due to its wide band gap (3.2 eV) and high chemical stability. It has high optical transmittance and offers radiation shielding properties. TiO_2 is a suitable alternative to WO_3 in similar optical and photocatalytic applications and is generally less expensive [55].

Zinc oxide (ZnO)

ZnO has a wide band gap (3.37 eV) and high photocatalytic activity. It has high optical transmittance and is used in biomedical applications due to its antimicrobial properties. ZnO can be an alternative to WO_3 with its high photocatalytic efficiency and advantages in biomedical applications [44].

Cerium oxide (CeO_2)

With its unique redox properties, CeO_2 exhibits high photocatalytic activity and provides radiation protection. It is also valuable in biomedical applications due to its antioxidant properties. CeO_2 is a powerful material as a photocatalyst and radiation shield. It also stands out with its antioxidant properties in biomedical applications [41]. V_2O_5 has photocatalytic activity and offers electrochromic and energy storage properties. It is used as a cathode material in lithium-ion batteries. V_2O_5 offers photocatalytic and electrochromic properties similar to WO_3, and is also advantageous in energy storage applications.

Tritium (T)

As a result of atomistic simulations, the permeability of tritium was determined to be higher in WO_3 compared to W and WO_2, and it was observed that there was a negative discrimination on WO_3 surfaces in the high coverage area [56]. It was concluded that WO_3, which has radiation protection properties, increased WO_3 content in TeO_2-TiO_2-WO_3 glass systems increased the protection against gamma radiation and fast neutrons [57]. It was confirmed by scanning tunneling microscopy and X-ray photoelectron spectroscopy. WO_3 can form monodisperse cyclic trimers (WO_3) 3 on TiO_2 (110) surfaces. These different properties and applications make WO_3 play an important role in many areas ranging from medical diagnosis to radiation protection and surface science [55].

PRODUCTION OF TUNGSTEN OXIDE NANOFIBERS BY ELECTROSPINNING

To form a composite using PVA (Polyvinyl alcohol) and PVP (Polyvinylpyrrolidone) with WO_3, PVA and PVP are first dissolved separately in distilled water at certain concentrations. PVA solution is usually prepared by heating at 70-80°C, while PVP solution is dissolved at room temperature or by gentle heating. At the same time, WO_3 nanoparticles are dispersed in pure homogeneous water or alcohol with the help of an ultrasonic bath or magnetic stirrer. Then, PVA or PVP solutions are combined in the desired proportions and mixed until a homogeneous mixture is obtained. Then, WO_3 dispersion is slowly added and the mixture is further processed using an ultrasonic bath for uniform distribution of nanoparticles. Uniform distribution of WO_3 in the solution is important in order not to disrupt the morphology of the fibers. The viscosity of this prepared polymer/WO_3 solution is adjusted to the appropriate level for the electrospinning process. If the viscosity is too low, droplets may form and if it is too high, spraying becomes difficult, so the correct viscosity is a critical step. Fiber production from the prepared solution is done using an electrospinning device (Figure 6) [58].

The syringe containing the solution is connected to a metal needle to which a high voltage (usually 10-30 kV) is applied. The high voltage creates electrical forces on the surface of the solution, causing the solution to exit the needle in a fine spray and form fibers. As the solvent of the sprayed solution evaporates rapidly in the air, fine fibers form on the collector surface. The collector can usually be a flat surface covered with aluminum foil or a rotating cylinder. Finally, these fibers are dried at room temperature or by gentle heating, and if necessary, their mechanical properties are strengthened by heat treatment. The resulting WO_3/PVA/PVP composite fibers can be used in various areas such as sensors, optical devices and biomedical applications. The electrospinning method is frequently preferred in nanotechnology and advanced material applications because it provides advantages in obtaining high surface area and porous structures.

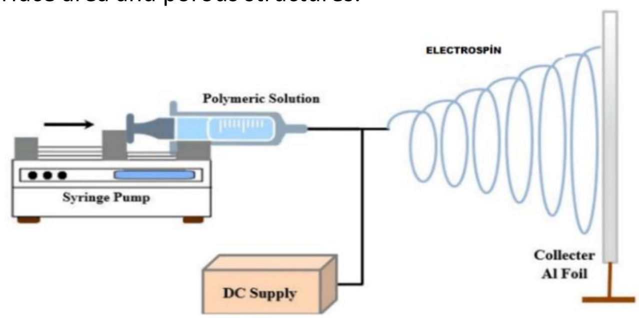


Fig. 6. Production stage of electrospinning [58]

CONCLUSION

WO_3 can act as a trap for radioactive isotopes. For example, studies on the permeability of WO_3 to tritium (T) suggest that this material has the potential to provide long-term stability and activity in radioactive environments. This supports the use of WO_3 in environments with radiation risks, such as nuclear power generation and space technology [55–57].

Furthermore, WO_3-doped thin-film transistors have been shown to exhibit high stability and excellent electrical performance even under high ionizing radiation. The presence of tungsten suppresses radiation-induced anomalous increases in conductivity and oxygen vacancy concentration, making 4% WO_3-doped devices reliable for use in radiation-prone environments such as nuclear energy and space technology, offering more effective and lightweight solutions than radiation shielding. Furthermore, WO_3 shows superiority in radiation attenuation parameters and optical and mechanical properties. When combined with polymers such as PVP or PVA, gamma radiation attenuation performance increases with increasing WO_3 content.

Tungsten oxide also acts as an effective radiation shield when incorporated into glass composites. Increasing the WO_3 content improves the optical properties and radiation attenuation capabilities of these glasses. WO_3 nanoparticles also serve as suitable dose enhancers for various radiation therapies, making them an important material in biomedical applications.

Peer-review: Externally peer-reviewed.

Author Contributions: Concept – A.K.; Supervision – A.K.; Data Collection and/or Processing – E.G.; Analysis and/or Interpretation – E.G.; Literature Search – E.G.; Writing Manuscript – E.G.; Critical Review – S.D.

Conflict of Interest: The authors have no conflicts of interest to declare.

Financial Disclosure: The authors declared that this study has received no financial support

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