



Article Investigation on Physico Chemical and X-ray Shielding Performance of Zinc Doped Nano-WO₃ Epoxy Composite for Light Weight Lead Free Aprons

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Abstract: This report addresses a way to reduce the usage of highly toxic lead in diagnostic X-ray shielding by developing a cost-effective, eco-friendly nano-tungsten trioxide (WO_3) epoxy composite for low-weight aprons. Zinc (Zn)-doped WO₃ nanoparticles of 20 to 400 nm were synthesized by an inexpensive and scalable chemical acid-precipitation method. The prepared nanoparticles were subjected to X-ray diffraction, Raman spectroscopy, UV-visible spectroscopy, photoluminescence, high-resolution-transmission electron microscope, scanning electron microscope, and the results showed that doping plays a critical role in influencing the physico-chemical properties. The prepared nanoparticles were used as shielding material in this study, which were dispersed in a non-water soluble durable epoxy resin polymer matrix and the dispersed materials were coated over a rexine cloth using the drop-casting method. The X-ray shielding performance was evaluated by estimating the linear attenuation coefficient (μ), mass attenuation coefficient (μ _m), half value layer (HVL), and X-ray percentage of attenuation. Overall, an improvement in X-ray attenuation in the range of 40-100 kVp was observed for the undoped WO₃ nanoparticles and Zn-doped WO₃ nanoparticles, which was nearly equal to lead oxide-based aprons (reference material). At 40 kVp, the percentage of attenuation of 2% Zn doped WO₃ was 97% which was better than that of other prepared aprons. This study proves that 2% Zn doped WO₃ epoxy composite yields a better particle size distribution, μ_{m} , and lower HVL value and hence it can be a convenient lead free X-ray shielding apron.

Keywords: Zn/WO₃ nanoparticles; epoxy-nano composite; lead free aprons; physical characterization; X-ray attenuation analysis

1. Introduction

It is known that numerous clinical personnel are exposed to diagnostic radiation every day [1]. Exposure to radiation at a certain level causes serious issues for human beings. Long-term exposure to radiation above the safety level or without appropriate productive gear may cause serious and fatal effects such as cancer, cell damage, and other undesirable health issues [2]. Lead (Pb) is the traditional material used in aprons which acts as radiation shielding material for clinical operators due to its high atomic density and high X-ray attenuation co-efficient [3]. However, Pb poses a serious threat to human health, especially infants and it is very difficult to recycle and store. The incorporation of lead oxide nanoparticles onto a polymer matrix creates a nanocomposite material that is more robust and requires less maintenance. Consequently, the content of lead used in shielding material would lessen. The polymer matrix acts as a protective layer around



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the nanoparticles, shielding them from external stresses. Some researchers have found that Pb-based dimethyl polysiloxane, polystyrene and polystyrene-b-polyethyleneglycol composite materials yield better attenuation than pure Pb [4–7]. As a result of the European Union's prohibition of the use of Pb in European healthcare, we increased the urgency of replacing Pb-based aprons with those made of alternative materials [1]. So, along with Pb, other materials such as bismuth and tungsten related compounds were investigated as radiation shielding material due to their high atomic number (z) [8]. Among them, tungsten is a material of choice with a high X-ray attenuation coefficient, high k-absorption edge, and the lowest degrees of toxicity [8]. In addition, tungsten oxide is a much safer material and more delicate to use in diagnostic radiation aprons [9]. However, to improve the chemical and physical stability, tungsten derivatives such as tungsten oxide can be considered as an alternative material for effective X-ray shielding. This material is inexpensive, easily viable and includes other advantages such as low toxicity, recyclability and safe storage capability compared with toxic Pb. Considering all these factors that are to be prioritized for humans, tungsten oxide would be the best choice to replace toxic lead.

In the ideology of lead-free aprons, polyvinyl alcohol (PVA)-based micro and nanocomposites have been used in X-ray and gamma ray shielding in recent times. Studies have used PVA blended molybdenum nanoparticles, tin oxide, silver chloride and tungsten trioxide in X-ray and gamma ray blocking materials and the results are acceptable [10,11]. Similarly, there is a sustainable effect observed on electrospun PVA-based nanofibers filled with bismuth oxide and tungsten trioxide as a radiation shielding material [9]. In other polymers such as polyethylene, nature rubber, isophthalic resin, poly dimethyl siloxane, polyboron, epoxy resin, methylsilsesquioxane, and fiber plastic [12]. At present, researchers are focusing on lead-free metal oxides polymer composites such as polymethyl-methacrylate matrix filled with bismuth oxide (Bi_2O_3), bismuth (Bi) and tungsten (W) composite, Bi_2O_3 , tungsten trioxide (WO₃), tungsten carbide (W_2C), tantalum pentoxide (Ta_2O_5) filled with polypropylene prepared by three-dimensional needled shielding fabric and epoxy doped zinc oxide (ZnO) [13–16]. The epoxy resin was chosen in this work as an alternative dispersion medium owing to it is readily available and easily scalable [17]. The epoxy resin is thermosetting polymer structure-based epoxy which is cross-linked to form a highly rigid and durable network structure [18]. It is also durable compared to other polymers with high mechanical properties, easy processing with low shrinkage during the casting process [19]. In addition to that, epoxy is a thermoplastic which can withstand higher temperatures, making it a suitable material for power washing [19]. For the final part of the preparation of aprons, a thin nylon supported rexine cloth was used to increase its reusability with low wear and tear [20]. The rexine and epoxy combination offer an excellent adhesion to one another with a strong binding tendency [21]. Compared to the other fibers, the low porosity of rexine offers a good sealing property which also protects the epoxy—nanoparticle composites and prevents from the damage of skin by blocking the radiations.

Using micro-particles instead of nanoparticles with the epoxy as a compound layer results in less homogeneous, void development in the aprons [22]. By reducing the particle size and shrinking them, we can address this problem [23]. Therefore, innovative lead-free radiation protection materials can be created using the special doped nanomaterials characteristics associated with nanomaterials [24,25]. The size lowered nanoparticles especially based lead-free aprons exhibit good scattering and improved absorption of secondary X-rays [26]. The addition of a dopant can change the effective atomic number (Zeff) of the composite material, which can affect its X-ray shielding properties. Hence, in this work, we used nanoparticles of Zn-doped WO₃ as dispersion, epoxy as a composite layer, and nylon supported rexine as a base layer for the fabrication of the apron. The variation in the concentration of Zn (1%, 2%, 3%) in the WO₃ matrix alters the physical properties of WO₃ [27], which are studied for the application of X-ray shielding in this work.

2. Materials and Methods

2.1. Synthesis of Zn-WO₃ Nanoparticles

WO₃ nanoparticles were prepared through the acid-precipitation method [28]. First, sodium tungstate dihydrate (Na₂WO₄·2H₂O) was dissolved in 600 mL of double distilled water. In this solution, 0.0, 1.0, 2.0, and 3.0 mol% of zinc chloride (ZnCl₂) was added, and hydrochloric acid (HCl) was added dropwise until the pH of the medium turns 1. After adding HCl, the solution was turned yellow in color which indicated the formation of tungstic acid (H₂WO₄). Then it was allowed to age for 24 h at room temperature under normal stirring and subjected to sonication. The precipitate was collected by centrifugation and washed with the help of distilled water to remove sodium chloride (NaCl), which was shown in the chemical reaction (R2). The precipitate was calcinated at 500 °C and H₂O got evaporated, which was given by the chemical reaction (R2) [29].

$$Na_2WO_4 \cdot 2H_2O + 2HCl + H_2O \rightarrow H_2WO_4 + 2NaCl + 3H_2O$$
(R1)

$$H_2WO_4 + 3H_2O \xrightarrow{\Delta} WO_3 + 4H_2O \uparrow_{(g)}$$
 (R2)

Finally, the calcinated product was ground for further characterization and apron fabrication. The 0.0, 1.0, 2.0, and 3.0% Zn doped samples were labeled as WZ0, WZ1, WZ2, and WZ3 respectively hereafter.

2.2. Fabrication of Zn-WO₃ Nanocomposite Apron and Measurement Set-Up

The filler (prepared nanoparticles) and epoxy polymers were mixed in a 1:1 ratio weight percentage using a magnetic stirrer and uniformly dispersed. A glass cuboid template with a dimension of 4 cm \times 4 cm was placed over a rexine cloth. The nanocomposite was spread using the drop-casting method over the rexine cloth to mimic the fabric of the apron. It was allowed to rest for 12 h at room temperature and the desired study material was acquired. This preparation process for the apron is shown in Figure 1a,b, respectively.



Figure 1. (a) Schematic representation of the fabrication process. (**b**–**e**) Prepared WZ0, WZ1, WZ2, and WZ3 epoxy nanocomposite-based aprons used for X-ray shielding studies. (**f**) Graphical depiction of X-ray attenuation study.

A sample size of 4 cm \times 4 cm was kept over a sample holder made up of lead with an opening of 3 cm \times 3 cm at the center. The sample and detector were located at 50 cm and 100 cm respectively from the X-ray source [30]. A lead box was placed behind the sample enclosing the detector to prevent the scattering of X-rays. The exposure was set at 10 mAs, time was set at 2 s and the X-ray tube voltage was between 40 and 100 kVp. An X-ray beam of 1 cm \times 1 cm width from the X-ray source was allowed to pass through the sample. The penetrated radiation was received by the detector and read from the display.

2.3. Characterization

The structural properties were identified using the model Empyrean, Malvern Panalytical Powder X-ray Diffraction (XRD) instrument (Malvern, UK) using the Cu K_{α} source $(\lambda = 0.154 \text{ nm})$. The optical properties of prepared samples were analyzed through UVvisible (UV-Vis) optical spectrometer using the model Jasco V770, 28600 mary's court Easton, MD, USA 21601. The defect and local structural properties were confirmed and analyzed through photoluminescence (PL) and Raman scattering studies using the perkins Elmer LS45 (Ulm, Germany), and WiTec alpha 300 (355 and 532 nm laser) (Ulm, Germany) respectively. The surface morphology, elemental analysis, and elemental mapping were carried out by EVO 18 model's scanning electron microscope (SEM) (Jena, Germany) and energy dispersive X-ray spectroscopy (EDX) (Jena, Germany) studies respectively. The fine structure such as lattice planes, grain size, and selected area diffraction (SAED) was carried out by high-resolution transmission electron microscope (HR-TEM) model JEOL JEM 2100 (Peabody, MA, USA). For X-ray attenuation studies, M/S Wipro Ge Healthcare's fixed radiography model HF (Banglore, India)advantage was used for producing a 40–100 kV X-ray source with an average exposure time of 2 s and the source to image distance (SID) of 100 cm [30,31] detected using the RTI Piranha 557 electrometer (Molndal, Swedan).

3. Results

3.1. XRD Analysis

XRD analysis was performed to investigate the crystalline size, crystal structure and lattice characteristics of Zn-doped WO_3 nanopowders. Table 1 shows the crystalline structure of prepared nanoparticles. Figure 2a shows the X-ray diffraction patterns of pure WO₃ and Zn-doped WO₃ nanopowders annealed at 500 °C. The XRD result shows major intense peaks at 23.1°, 23.5°, 24.3°, 26.6°, 33.2°, 33.5°, 34.1° and 49.9° which correspond to the planes of (002), (020), (200), (120), (022), (-202), (202) and (140) respectively. These planes match well with the JCPDS card No: 71-2141 and confirm the formation of monoclinic WO_3 particles [32]. The prominent peak of WZ0 is located at (200) direction. The direction of the prominent peak changed when the dopant is introduced. Zn prefers to locate in the (120) direction for the samples WZ1 and WZ2. WZ3 peak is located at the (002) direction. For pure WO_3 particles, the lattice parameters have been calculated as a = 0.732 nm, b = 0.750 nm, and c = 0.768 nm from Equation (1) [33], which was also in good agreement with the standard data. Upon doping, the peak positions remain the same with negligible shift but the intensity changes with respect to the dopant concentration since the zero presence of additional peaks belong to elemental or compound impurities, which shows that there is no secondary phase formation or elemental impurity presence in the prepared samples. The crystallite size (D), cell volume (v), dislocation density (δ) and the micro strain (ϵ) are calculated using Equations (1)–(5) [33,34].

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$
(1)

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

where, d—interplanar distance, a, b, c—lattice parameters, hkl—miller indices, β —full width half maximum (FWHM) and k—Scherrer constant.

$$V = abc \, \sin\beta \tag{3}$$

$$\delta = \frac{1}{D^2} \tag{4}$$

$$\varepsilon = \frac{\lambda}{D\,\sin\theta} - \frac{\beta}{\tan\theta} \tag{5}$$

where, θ —pea	ik position and	l λ—X-ray wave	length (Cu	$k_{\alpha} = 0.1514 \text{ nm}$).
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Sample	Lattice Parameters (Å)			Cell	Crystallite	Dislocation	Micro Strain (ε)	Texture	Stacking
Sample	а	b	с	Volume (Å ³)	Size (nm)	Lines m ⁻²	\times 10 ³ Lines ² m ⁻⁴	(TC _(hkl))	Fault
WZ0	7.32	7.50	7.68	422	29.2	1.19	1.73	1.08	0.37
WZ1	7.27	7.56	7.70	424	12.9	5.96	2.65	1.58	0.75
WZ2	7.29	7.47	7.72	421	11.9	6.95	2.86	2.08	0.82
WZ3	7.28	7.48	7.71	420	16.3	3.75	2.09	0.63	0.70



Figure 2. (a) XRD spectra of undoped and Zn doped WO₃ nanoparticles. (b) Crystallite size Vs dislocation density correlation. (c) Raman spectra of WZ0, WZ1, WZ2, WZ3 nanoparticles.

The changes in lattice parameters are due to different concentrations of doping and are given in Table 1. This is due to the incorporation of Zn ions into the WO₃ lattice matrix where it alters the crystalline properties of the WO₃ nanoparticles [35]. From the XRD result, it is evident that doping causes the structural parameters to change. Especially the sharp increase in intensity of the peak (120) shows less crystallite size for 2% doping, owing to the smaller ionic radii of Zn²⁺ (0.074 nm) ions compared to W⁶⁺ ions (0.078 nm) [27]. Causes the charge imbalance in lattice planes and alters the interplanar distance. This change in interplanar distance causes other parameters to deviate, resulting in an improved crystallite size. For increased Zn concentrations, crystallite size is found to be slightly greater than 2% but smaller when compared to a pure sample. Among all the samples, WZ2 exhibits better crystalline quality than other prepared materials. Figure 2b shows the crystallite size vs dislocation density trend for various Zn dopant concentrations in the WO₃ matrix. Using

Table 1. Crystalline properties of WZ0, WZ1, WZ2 and WZ3 nanomaterials.

the formula below, we are able to determine the stacking fault (SF) and texture coefficient (TC) [36,37].

$$SF = \frac{2\pi^2}{45(\tan\theta)^{1/2}} \beta$$
(6)

$$TC_{(hkl)} = \frac{[I_{(hkl)}/I_{0(hkl)}]}{\Sigma N[I_{(hkl)}/I_{0(hkl)}]} \times 100\%$$
(7)

where, N is the number of diffraction peaks, $I_{(hkl)}$ and $I_{0(hkl)}$ are the measured relative intensity of a plane and the standard intensity of the plane, taken from JCPDS data. The TC value is varied for different doping concentrations. The sample WZ2 has the highest TC value which indicates that it has plenty of closely oriented crystallites and the lowest TC value of the sample WZ3 represents that it possesses randomly oriented crystallites. The fluctuation of SF is caused by the formation of crystal defects. The presence of SF in a crystal produces a shift in the phase of incident and scattered X-rays with regard to the lattice, altering the consequent peak location. As WZ0 has the highest crystalline size, SF is low. When dopant is introduced, the crystalline size is reduced resulting in an increase in SF. Among the samples, WZ2 is associated with the highest SF value (Table 1). These properties of WZ2 make it a better X-ray attenuation material.

3.2. Raman Analysis

Figure 2c shows the Raman spectra of prepared pure WO_3 and Zn-doped WO_3 (WZ0, WZ1, WZ2, WZ3) nanoparticles. Table 2 shows the Raman spectra peak position of prepared nanoparticles. The pure WO_3 particles exhibit intense peaks at 81, 131, 188, 272, 326, 713, and 807 cm⁻¹. In general, the observed peaks from 200 to 500 cm⁻¹ and from 600 to 1000 cm^{-1} represent the O-W-O bending modes and W-O stretching modes of the WO₃ system respectively. Peaks below 200 cm^{-1} are attributed to the translational or rotational lattice modes in WO₆ octahedron [32,38]. Among these, the peaks at 81 and 131 cm⁻¹ correspond to the vibration of W_2O_2 chains which is a unique mode of the monoclinic phase of WO₃ nanoparticles [32]. The peaks at 713 and 808 cm⁻¹ represent the stretching vibration of O-W-O ions [39]. This is in good agreement with the XRD results and confirms the formation of monoclinic WO₃ particles. The peaks at 272 and 326 cm⁻¹ reveal the plane bending vibration of the O-W-O ions [39]. Upon doping of Zn ions into a lattice, the peak positions show negligible shifts and a sharp change in intensity. The negligible peak position shift may originate from several factors such as a laser-induced heating effect or morphological changes in the focusing point [34]. The observed results reveal the complete dissolution of Zn ions into the WO₃ lattices. The change in the Raman peak intensity is ascertained by Zn doping effect.

Samples			Pe	ak Position (cm	-1)		
WZ0	81.8	131.8	188.8	272.3	326.8	713.5	807.7
WZ1	80.8	131.5	188.3	270.4	326.3	713.7	807.7
WZ2	80.8	133	190.7	270.4	326.8	715.9	809.7
WZ3	76.5	136	186.7	272.5	326.3	713.7	807.7

Table 2. Raman spectra peak analysis of Zn doped WO₃ particles (WZ0, WZ1, WZ2, WZ3).

3.3. Optical Properties

The optical properties of pure WO₃ and Zn-doped WO₃ nanoparticles were explored using UV-Vis-DRS spectra. The DRS spectra of the prepared nanoparticles manifest strong band edge absorption in the UV-Vis region. All the samples exhibit their band edge absorption between 320 to 345 nm (shown in Figure 3a), which might be due to the intermolecular charge transfer or to the conjugation system [40]. The sharp absorption peak between 320 to 345 nm shows the well crystalline quality of all the samples [41,42]. All the Zn-doped WO₃ nanoparticles are blue-shifted when compared to the WZ0 sample,

which confirms that the optical properties of WO₃ nanoparticles are highly influenced by Zn doping [43]. Using the Kubelka–Munk plot (Figure 3b), the optical bandgap is estimated to be 2.88 eV at room temperature for WZ0. The optical bandgap energy of doped samples namely WZ1, WZ2, and WZ3 is higher than that of the pure WZ0 nanosystem, the energy gap values of the samples are calculated as 3.01 eV, 3.09 eV, and 2.97 eV respectively. This result reveals that the Burstein–Moss effect plays a major role [44]. The doping of semiconductor materials moves the fermi level beyond the conduction band due to the formation of a larger number of donor levels [45]. Hence the bandgap obtained from such doped material is found to be enlarged. For the doped oxide nanoparticles, the optical bandgap energy variation is owing to the synergetic effect betwixt Zn and WO₃ [33,43]. The values are consistent with the reported value [46]. Urbach energy (E_u) is known as the width of the defect bands, which are produced by the charge disproportionation, and creates an impact on the optical transitions betwixt the valance and conduction bands as well. These defect bands introduced the Urbach tail or localised states in band tails. E_u is the term for the energy connected to this defect tail. These defects may also have developed throughout the development process, leading to lattice abnormalities and stress in the sample. The E_u has been calculated by taking the inverse of the slope of the equation [47].



$$\ln \alpha = \ln \alpha_0 + h\upsilon / E_u \tag{8}$$

Figure 3. (a) UV-Vis absorption spectra of synthesized WZ0, WZ1, WZ2, and WZ3 nanoparticles. (b) Kubelka–Munk plot for the synthesized nanoparticles (Figure insert: Variation in bandgap vs. maximum absorption wavelength). (c) Urbach energy Vs strain plot. (d) PL spectra of synthesized nanoparticles of undoped and Zn doped WO₃ (WZ0, WZ1, WZ2, WZ3) system.

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The creation of defect levels in betwixt the band gaps obviously enhances the E_u with Zn dopant. A higher E_u shows that the sample WZ2 is more prone to transform weak bonds into defects [48]. This is also consistent with the strain behaviour reported in XRD studies (Figure 3c).

The defect properties of prepared nanoparticles were investigated using photoluminescence (PL) spectra at room temperature. The excitation wavelength of the PL spectrum is 355 nm. The WO₃ nanoparticles at various dopant concentration levels exhibit three emission bands as shown in Figure 3c. The PL spectra for both WO_3 and Zn-doped WO_3 nanoparticles showcase similar emission bands and dopants do give or raise any new peaks from PL phenomena. However, the intensity of dopant materials (WZ1, WZ2, WZ3) is found to be reduced compared to WZ0. The sharp and high-intensity peak centred at 365 nm (3.39 eV) corresponds to the ultraviolet (UV) band. It is due to the recombination of electrons from the internal states of the charged oxygen vacancies in the conduction band to the valence band [49,50]. WZ3 material has a strong emission band at the wavelength of 365 nm (3.39 eV) originating from higher content of surface oxygen vacancy. Due to this vacancy, the WZ3 material has less crystallinity compared with WZ0 [33,51]. The second emission band was observed as blue emission of 449 nm (2.76 eV) which may be attributed to the presence of radiative recombination betwixt the bandgap energy of 2.76 eV or oxygen vacancy defect in WO₃ [52,53]. The third emission band for the samples WZ0, WZ1, WZ2, and WZ3 are located at 522, 517, 513, and 521 nm respectively. The low intense and broad peak is related to green band emission caused by the presence of interstitial oxygen vacancy. The oxygen defects or vacancy gives rise to the green colour for WO₃ nanoparticles rather than its native yellow colour [54]. While increasing the Zn dopant concentration from WZ1 to WZ2 the intensity of the green emission peak decreases and shifts to a lower wavelength. Further increasing the Zn concentration, the intensity of the green emission becomes raised, and position of the peak is shifted to a higher wavelength region. This phenomenon is ascertained by the deep defect level present in the material WZ3 [33,55]. It is noteworthy that, after dispersing the WO_3 nanoparticles in the epoxy resin, the colour of the WO_3 changes much dark and turns bluish-grey in colour. The change in colour is assumed as epoxy reacts with WO₃ nanoparticles and there may be a bond formation between epoxy and WO₃ nanoparticles. This will give rise to strong structural integrity.

3.4. HR-TEM and SAED Analysis

Figure 4a shows the TEM image of WZ0nanoparticles with agglomerated pseudocuboid morphology which may become clustered together during the growth and annealing process. The larger particles are anchored by the smaller particles on the surface, such agglomeration and clustering are common limitations in the solution-grown nanoparticles [28]. The particle size distribution plot for Figure 4a shown in Figure 4c conveys the poly-dispersed state of the nanoparticles. i.e., the size of the larger particles was in the range of 300–700 nm and the size of smaller particles adhered on the surface of the larger particle was in the range of 20–100 nm. This smaller particle anchoring on the larger particle can be seen clearly in Figure 4a. The TEM micrograph of WZ2 nanoparticles showcased the distinct and agglomeration-free state. The doping of Zn into WO₃ reduces the overall size of the nanoparticles (Figure 4d) compared to WZ0. The average size distribution of the particles in the WZ2 sample is found to be 10-50 nm. It is also witnessed that medium-size particles are in the range from 60–250 nm and with aggregated particles are in the range of 300–400 nm (Figure 4f). Also, upon doping, the morphology of the particles transformed from cuboid shape to cube and rods with uneven edges. The WZ2 shows well-defined lattice fringes in Figure 4e. The incorporation of Zn into the WO₃ monoclinic system orients the crystallites into a single direction and limits the poly crystallization of WO_3 . Also, the 2% Zn doping improves the crystalline quality of the particle which is in good agreement with the XRD analysis findings.



Figure 4. (**a**,**b**,**d**,**e**) TEM micrographs of WZ0 and WZ2 nanoparticles. (**c**,**f**) Histogram of particle size distribution.

Figure 5a–f shows the SAED pattern images of undoped WO₃ and 2% Zn doped WO₃ nanoparticles obtained from HR-TEM. The inverse contrast image of the SAED pattern clearly distinguishes the pure and doped WO₃. In the pure WO₃, the dot patterns are arranged precisely with high periodicity, on the other hand, the doped one exhibits less distorted spots. The observation clearly demonstrates the differences in the lattice property of the Zn-doped lattice from the pure WO₃. Overall, the result proves the formation of monoclinic WO₃ and the incorporation of Zn ions into the WO₃ lattice does not alter the monoclinic structure of WO₃.



Figure 5. (**a**,**d**) TEM micrographs of WZ0 and WZ2 samples. (**b**,**e**) hkl indexed dot pattern of WZ0 and WZ2 samples. (**c**,**f**) Inverse contrast applied the SAED pattern of WZ0 and WZ2, respectively.

3.5. SEM-EDAX Analysis

The cross-sectional view of WZ0 and WZ2 impregnated epoxy-resin aprons was subjected to SEM and elemental mapping analysis and the results are shown in Figure 6a–j. The presence of carbon in the elemental mapping is reasoned for the rexine cloth. Zn, W, O are also witnessed in the study which confirms the formation of compound Zn doped WO₃. Figure 6h–j confirms the even distribution of Zn, W, and O elements in the apron in the form of Zn-doped WO₃ nanoparticles.



Figure 6. (**a**–**j**) SEM mapping of WZ0 and WZ2 apron cross-section. (**k**,**l**) EDS spectra and the weight composition of WZ0 and WZ2 samples.

Figure 6k,l shows the EDS spectra of WZ0 distributed apron and WZ2 impregnated epoxy-rexine apron. The spectra show the presence of carbon, tungsten, and oxygen. The peak of carbon is originated from the rexine and epoxy. Zn, W and O peaks in the spectra confirmed that Zn is doped in the WO₃ lattice. The apron with a low concentration of Zn exhibits a less intense peak. The other small peaks presented in EDS are attributed due to the rexine and epoxy compound materials.

3.6. X-ray Shielding Analysis

Much experimental evidence for the interaction of X-ray photons with matter are available in literature starting from Thomson scattering to Compton scattering. Many researchers have realised that their works reveal either absorbed (or) scattered (or) attenuated matter. In the energy range, below 200 kVp, the photoelectric effect (PEE) is the predominant phenomenon of X-rays that is accompanied by characteristic radiation, photoelectrons, and positive ions. Above 200 kVp, Compton scattering comes into existence with X-ray photons [56]. In the present study, employed diagnostic X-rays are in the energy range of 20–140 kVp which is primarily used in the angiographic, orthopaedic and dental X-ray imaging processes [33]. To estimate the innate attenuation of X-rays by the rexine and epoxy resin, X-ray attenuation studies were performed on the pure epoxy coated over a rexine cloth. The results show that (Figure 7a,b), the epoxy rexine layers have linear attenuation throughout the 40–100 kVp range. The epoxy shows higher X-ray attenuation than the bare rexine cloth. The prepared WZ0, WZ1, WZ2, and WZ3 nanoparticles are separately dispersed uniformly in the epoxy resin under vigorous stirring and coated

over the rexine cloth via the drop-casting method. Though a wide variety of aprons are commercially available in market, by following the same experimental protocol we prepare a PbO impregnated epoxy resin–rexine cloth apron as a reference material. The X-ray attenuation percentage is evaluated from the relation below [31]

 $%Attenuation = \frac{Electrometer reading without sample - Electrometer reading with sample}{Electrometer reading without sample} \times 100\%$ (9)



Figure 7. (a) X-ray attenuation percentage of pure epoxy and rexine cloth. (b–f) explain the attenuation percentage, HVL, Exposure, μ and μ_m analysis of WZ0, WZ1, WZ2, WZ3 and PbO-based aprons respectively.

The WZ0, WZ1, WZ2, and WZ3 nanoparticles-based apron and the PbO-based apron show similar trends in X-ray attenuation performance over the entire test range. This trend is maintained in the X-ray attenuation at higher tube voltages, especially between 70 and 100 kVp. A slight increase in the attenuation value of a Pb-based apron is attributed to its high atomic number (Pb = 82) compared to tungsten (W = 74), but the difference in X-ray attenuation between the prepared aprons is less significant in real-world operation [8]. Also, contrary to expectation, among the Zn-doped WO₃ system-based apron, WZ2 performed well in the X-ray attenuation of WZ2 is better than that of PbO for lower tube voltage (40–50 kVp). Besides, Half-Value-Layer measurements are also made for the prepared aprons, the numerical value of the HVL is found using the relation (10) and (11), which is also an important parameter to estimate the X-ray attenuating apron [8]. It is also interesting to notice that HVL is the thickness of the sample adequate enough to reduce the initial intensity of the X-rays into half [57,58].

$$HVL = \frac{0.693}{\mu} \tag{10}$$

$$\mu = -\frac{1}{t} Ln \left(\frac{I}{I_o} \right) \tag{11}$$

$$\mu_{\rm m} = \frac{\mu}{\rho} \tag{12}$$

$$\rho = \frac{m1}{m1 - m2}\rho_1 \tag{13}$$

where, µ–Liner attenuation coefficient, t—thickness of the sample, I—intensity of attenuated beam and I_o —initial intensity, μ_m —mass attenuation coefficient, ρ —density of the material (density of unknown materials was calculated by the Archimedes method), m1—mass in air, m2—mass in immersion liquid and ρ_l is the density of the immersion liquid (here, ethanol is immersion liquid $\rho_{\rm l} = 0.789 \text{ g/cm}^{-1}$). From the results (Figure 7c), WZ2 showed a low HVL value for a low energy range of 40–50 kVp of tube voltage. Beyond which, it is found that the value of HVL increases linearly throughout the voltage range. The prepared aprons WZ0, WZ1 and WZ3 also showed a similar trend of increasing HVL values. All the samples exhibit a higher value than the Pb based apron. The sample WZ2 shows low HVL for the energy range 40-50 kVp and starts to increase exponentially for the energy range 50–100 kVp. It is noteworthy that, the value of the HVL of WZ2 based apron is higher for than the HVL value of PbO based apron in the higher energy range (80–100 kVp). Figure 7d represents the tube voltage vs exposure, which provides the information about quality of radiation reaching the detector after passing through the apron. It is understood that PbO and WZ2 have identical and lowest exposure among all the samples. After which the second lowest exposure is exhibited by WZ0 followed by WZ1- and WZ3-based aprons. The important reason behind the similar exposure of WZ2 and PbO in X-ray shielding is that the size effect of Zn-doped WO_3 nanoparticles compared to the micro-sized PbO particles in an apron. The uniform distribution of nanoparticles in the epoxy matrix is also attributed to similar exposure behaviour of PbO-based apron and WZ2-based apron [26]. Linear attenuation coefficient (μ) is calculated by Equation (11). If the thickness (t) of the material varies, μ might vary in the same material. It means, μ depends on the t of the given material. In the present study t of samples was not changed and Figure 7e shows the μ value for prepared WZ0, WZ1, WZ2, and WZ3 based aprons and PbO-based apron. At low tube voltage (40–50 kVp) WZ2 has a high μ value. As tube voltage increases further (50-100 kVp), μ of PbO was slightly more than that of WZ2 since in this energy region, photoelectric effect absorption is high for higher atomic number (Pb = 82) [59]. Also, μ of WZ2 is better than WZ0, WZ1, and WZ3. By dividing the μ by density (ρ), the resultant coefficient is ρ independent and is known as the mass attenuation coefficient (μ_m). The μ_m and ρ of the aprons are calculated by Equations (12) and (13), the ρ tabulated in Table 3. Figure 7f shows that WZ2 based apron had the highest μ_m value in lower tube voltage (40–50 kVp) and PbO marginally high in the higher tube voltage (50 kV–100 kVp). μ_m values of WZ0, WZ1 and WZ3 based aprons are lower than WZ2 based apron. Due to the photoelectric effect, the attenuation value dropped as photon energy increased in the low energy range (40–100 kVp) [60]. The comparison of $\mu_{\rm m}$ between the prepared sample and other polymer metal oxide composites and alloy materials is tabulated in Table 4. Figure 8 shows the reason for the better X-ray shielding property of WZ2 based apron than other aprons. Since there were no materials to block the X-ray, there was only 25% of the incident X-rays are attenuated (Figure 8a). The presence of pure WO_3 in the apron (Figure 8b) increases the attenuation up to 92%. There were no sufficient smaller-size particles in the pure WO₃ to block the X-rays. However, 2% Zn-doped WO₃ (Figure 8c) shows increased attenuation of 97% which is reasoned as a high amount of smaller-sized particles (10–50 nm) of WZ2 in WZ2 based aprons which seal the space between the largesized nanoparticles and epoxy resin fibers. Our report proves that doping Zn in a WO_3 matrix can alter the X-ray attenuation property of a material. The reduced particle size with improved crystallinity (obtained from TEM and XRD) of WZ2 also supports the above argument. The smaller the particle, the higher the grain boundary scattering probability coupled with the secondary scattering events, since, the number of particles per gram is greater compared to the lead particles [61–63].

Samples (with Epoxy Composite)	Thickness (10^{-3} m)	Density (g/cm ³)	
WZO	4.36	1.29	
WZ1	4.33	1.27	
WZ2	4.29	1.28	
WZ3	4.35	1.27	
PbO (reference material)	4.50	1.30	
Pure epoxy (Polymer)	4.15	1.05	

 Table 3. Composite Thickness and density of prepared aprons.

Table 4. X-ray attenuation performance comparison between tungsten oxide and different polymer composites shielding materials.

Material	Density (g/cm ³)	X-ray Energy (kVp)	Major Results	Reference	
SRM-50 (dimethyl polysiloxane + wt 50% PbO)	2.038	FO F1 1 00 00	HVL \approx 2 and 4	[4]	
SRN-50 (dimethyl polysiloxane + wt 50% PbO)	2.086	59.51 and 80.99	HVL \approx 2.5 and 3		
Portland Cement (89%) + PU-Plaster (1%) + Lead Oxide (10%)	-	121.78-1408.01	HVL \approx 30 and 125	[5]	
PS/PbO (A) 35	1.4015	40, 100	$\mu = 9.918 - 1.062$	[7]	
PS/PbO (B) 35	1.3560	40-100	$\mu = 9.829 - 1.440$	[/]	
B5 [(10% PVA) (WO ₃ Filler loading 40%)]	≈1.29	8.64–25.20, 57.53	$\mu_m \approx 155 - 25.20, 130$	[9]	
EPVC/micro WO ₃ 40 wt%		40 1100	μ _m = 11.20 and 5.49 HVL = 0.5 and 0.9	[0]	
EPVC/nano WO ₃ 40 wt%		40 and 100	μ _m = 11.81 and 5.68 HVL = 0.5 and 1	[0]	
WP1(W/polymer ration 300%)	-	150	$\mu_m\approx 3.5$	[64]	
Micro WO ₃ /E44 & Nano WO ₃ /E44	2.18, 2.29	59.6 $\mu_{\rm m} = 1.0196, 1.0706$		[65]	
W-SR (W wt 80%)	-	59.5	$\mu_m\approx 2.05$	[66]	
W0.115at%	-	40–100	$\mu_m\approx 0.34-0.24$	[19]	
PE-A-25 (PE 75%, TBG 25%) (TBG — nano WO ₃ + BI ₂ O ₃ + GO)	1.43	50-120	$\mu_m = 0.26 - 0.15$	[67]	
Wt 40% WO ₃ + PVA	1.79	5.89-59.54	$\mu_{\rm m} = 127.60 - 1.33$	[68]	
W	4.18		$\mu_{\rm m}$ = 8.74 and 5.25		
Sn-W	4.2	50 and 120	$\mu_{\rm m}$ = 9.89 and 5.71	[69]	
W-Ba	3.11		$\mu_{\rm m}$ = 9.51 and 5.55		
PVA + wt 40% WO ₃ (micro)		²⁰¹ Tl-radioactive	$\begin{array}{l} \mu_m \approx 0.98 \\ HVL = 3 \end{array}$	[70]	
PVA + wt 40% WO ₃ (nano)		sources	$\begin{array}{c} \mu_m \approx 1.28 \\ HVL = 2 \end{array}$	[70]	
WN400m	≈1.9	60–120	$\mu_m\approx 14.2-8$	[71]	
Epoxy + wt 50% PbO	1.30		$\begin{array}{l} \mu_m = 5.85 - 2.76 \\ HVL = 0.09 - 0.19 \end{array}$		
Epoxy + wt 50% WZ0 (undoped WO ₃ NPs)	1.29	40–100	$\label{eq:mm} \begin{split} \mu_m = 4.73 - 2.24 \\ HVL = 0.12 - 0.24 \end{split}$	Our work	
Epoxy + wt 50% WZ2 (2% Zn doped WO ₃)	1.28		$\label{eq:mm} \begin{split} \mu_m &= 6.54 - 2.66 \\ HVL &= 0.08 - 0.21 \end{split}$		

Units: HVL = mm, $\mu = cm^{-1}$, $\mu_m = cm^2 g^{-1}$.



Figure 8. Schematic diagram of X-ray attenuating property for (**a**) Rexine and pure epoxy composite, (**b**) Rexine and WZ0 epoxy nanocomposite, (**c**) Rexine and WZ2 epoxy nanocomposite.

Further, we presumed that the high surface to volume ratio of the nanosystem shows enhanced X-ray attenuation properties, since a greater number of WO₃ (or) Zn-doped WO₃ system are exposed themselves to incoming X-ray radiation. This phenomenon also greatly increases the chance of absorbing the X-ray photon which ends up with the blocking of X-rays. Thus, nanoparticle impregnation, in an either undoped (or) doped form improves the X-ray attenuation coefficient than (or) equal to PbO-based apron. There are several types of tungsten-based polymer composites that can be used for X-ray shielding; Table 4 compares their X-ray attenuation performance. Only minimal studies have been conducted on tungsten-based epoxy nanocomposite. In this study, Zn-doped WO3-based epoxy nanocomposite material is used for the first time to the best of my knowledge in an X-ray shielding application and the results are compared to other materials. Results show that the addition of a dopant enhanced the X-ray attenuation performance.

4. Conclusions

The X-ray shielding properties of Zn-doped WO₃ composite aprons were studied and discussed in detail. The pure and Zn-doped WO₃ nanoparticles were prepared using the acid preparation method. The XRD results show the crystalline nature with a monoclinic structure and reduction in crystalline size on the addition of Zn dopant, Raman vibration modes also confirmed the monoclinic structure. The optical study of UV-visble spectroscopy showed bandgap changes due to Zn doping. The addition of a dopant creates a defect in the parent material, which is shown by the photoluminescence study. TEM image revealed that the particle size of 2% Zn-doped WO₃ was smaller than undoped WO₃ and smaller particles in the 2% Zn-doped WO₃ were anchored to the larger particles, creating a better X-ray attenuation property by sealing the space between the large particles. The HVL of the 2% Zn-doped WO₃ system revealed less value and hence, it exhibited better attenuation in low-energy region. The study revealed that the WZ2-based apron had good mass attenuation coefficient (μ_m), which made it as an efficient material in X-ray shielding process. The results of the study demonstrate that doping can affect the X-ray attenuation efficiency of a material and that Zn doped WO_3 can be used as an alternative to lead for environmentally friendly and durable X-ray shielding applications.

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