Gamma Ray Irradiation Enhances the Linkage of Cotton Fabrics Coated with ZnO Nanoparticles

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ABSTRACT: In this work, we aim to study zinc oxide (ZnO)-based functional materials over cotton fabrics and their effects after gamma ray exposure of 9 kGy. We found that the binding of the nanoparticles with cotton fabrics can be enhanced after irradiation. This could be due to the oxygen deficiency or defects created in the interface between ZnO and cotton fabrics after irradiation. Near-edge X-ray absorption fine structure and X-ray photoelectron spectroscopy (XPS) were used to detect the oxygen inadequacies generated in the interior and at the surface of the ZnO nanoparticles after gamma ray exposure. XPS results showed that the binding energy of Zn shifts by 2 eV at 1.5 kGy and by 4 eV at 9 kGy. This huge shift of about 4 eV is completely different from other works due to the reaction that takes place on the interface between ZnO nanostructures and cotton fabrics after gamma ray irradiation. Overall, this work suggests that after gamma ray irradiation, there is an enhanced level of binding between the coated functional nanoparticles and cotton fabrics, which can be advantageous for the textile industries.

1. INTRODUCTION

Nowadays, functional clothes are of higher value in textile industries because of their enhanced properties and performance. For example, materials such as zinc oxide (ZnO) nanoparticles can be a useful electromagnetic interference-shielding material. Moreover, ZnO-coated cotton as a wearable cloth could be a potential application to protect human beings from high microwave absorptions. Previously, ZnO-coated cotton fabrics have been employed as a flame retardant agent. However, the interactions between ZnO and cotton have not yet been studied in detail. Gamma ray irradiation induces radical formation on materials, which is well known to cause cross-linking or chain scission. It is thus noteworthy to understand whether gamma ray irradiation on both cotton and ZnO nanostructures can enhance the linkage or dominate the scission process.

Primarily, textile substrates have been used on novel applications related to ZnO films. Cotton fiber usually contains many constituents. Among them, the cellulose content amounts to be around 88–96%. Riaz et al. discussed the applications of nanomaterials using flexible textile to obtain various functional properties, while Wang et al. gave an overview on the development in photocatalyst applications using modified textiles. Verbič et al. presented the usage of ZnO on a textile substrate for applications, such as flame retardancy, hydrophobicity, thermal insulation, and so forth. Recently, Gupta et al. have demonstrated that composites of reduced graphene oxide/zinc oxide over cotton fabric can be employed for the application of high microwave absorption. Although numerous applications on this material have been carried out, this kind of material still has a greater attraction in understanding the gamma ray exposure effects on cotton fibers.

In previous studies, most of the groups worked on the effects of protons, electrons, and gamma (γ) irradiations, and so forth on ZnO. The gamma irradiation technique has been useful in generating nanocomposites and nanoscale metals at room temperature. Moreover, this technique is adaptable, well...
controlled, and does not contribute impurities into the matrix. Reyhani et al. reported the effects of gamma irradiation on ZnO nanowires with various diameters. Although previous reports focused on explaining the variations in ZnO nanocomposites after gamma ray irradiations, their changes in the degradation mechanism and electronic and chemical structure modification, such as the binding between functional nanoparticles over coated cotton fabrics after gamma irradiations, have not been studied yet.

In this work, we aim to study the gamma ray irradiation effects on ZnO-based functional nanomaterials over cotton fabrics. We found an enhancement of linkage between the ZnO nanoparticles and cotton fabrics after gamma irradiation. To elucidate this novel result, X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), near-edge X-ray absorption fine structure (NEXAFS), X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible (UV-vis) spectroscopy were employed to assess the changes in the crystallinity and chemical and electronic structure of ZnO-based functional materials before and after gamma ray irradiations.

2. MATERIALS AND METHODS

2.1. Synthesis of ZnO Nanoparticles on Cotton Fabrics. ZnO nanoparticles were deposited on cotton textile fabrics based on the method reported by Jaber and Laanab. A piece of commercially available cotton fabric was used as a substrate. The density of the fabric was measured to be around 1.76 g/cm³. The fiber diameter is around 8.10 ± 1.70 μm, and it contains around 2000 fibers in a bundle. At first, the cotton fabric was washed with ethanol and dried in air. An aqueous solution of 0.1 M zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) was used as a zinc precursor, and the solution was heated at 60 °C. Subsequently, the cotton fabric was immersed in the solution. Then, the solution was heated again at 60 °C under continuous stirring. An aqueous solution of 1 M sodium hydroxide (12 mL) was slowly added in the solution under continuous stirring, and the reaction continued for 1 h at a constant temperature. The solution was cooled to room temperature. Then, the cotton fabric was washed ten times with deionized water to remove the excess precursor and subsequently dried. During the synthesis process, zinc ions have the ability to penetrate into the interior of the cotton fabric, finally resulting in the interaction of zinc ions with the hydroxyl groups of the cellulose molecular chain, leading to the formation of zinc-cellulose complex. These functional materials were then gamma ray irradiated by the ⁶⁰Co source at the radioisotope laboratory facility of National Tsing Hua University for a total dose of 1.5 and 9 kGy at a dose rate of 1 kGy/h. After gamma ray irradiation, the structural, optical, and electronic properties of the zinc oxide nanoparticles were evaluated using various characterization tools as explained below.

2.2. Characterization Techniques. The diffraction intensity and peak shifts, which are related to the crystallinity and structure change of ZnO nanoparticles, were investigated using Panalytical X’Pert Pro with Cu Kα (λ = 1.5406 Å) radiation over a 2θ range of 20°–40°. The morphologies of the nanostructures were then characterized by using FE-SEM (JEOL-6500F). The optical measurements were performed using a UV–vis spectrophotometer (Hitachi U-3900D). The changes in the electronic structure of ZnO nanoparticles before and after irradiation were studied at beam line BL-20A by utilizing the total electron yield mode at the Taiwan Light Source, National Synchrotron Radiation Research Center (NSRRC) facility. In order to analyze the change in the chemical states, oxidation, and distribution of the sample before and after irradiation, XPS was carried out at beam line BL-24A of the NSRRC facility.

2.3. Photocatalytic Self-Cleaning Test. The photocatalytic self-cleaning study of ZnO-coated cotton fabrics has been investigated by exposing the methylene blue (MB)-absorbed samples to ultraviolet light. For this purpose, bare cotton, pristine, and irradiated samples (1 cm × 1 cm) were immersed into 5 μM MB solutions and kept under mild stirring for 1 h. Then, these samples were dried at room temperature, and the self-cleaning property was further checked by exposing to an ultraviolet lamp (BLAK-RAY, 100 W) at a 15 cm distance. Optical images were taken at different time intervals of 0, 15, 30, 60, and 120 min.

Figure 1. Schematic representation of the experimental process for the synthesis of ZnO nanoparticles and the SEM micrograph.
2.4. Stability (Washability) Test. In order to determine the stability of the ZnO nanoparticles on cotton fabrics, the samples before and after irradiation were ultrasonicated for different time intervals of 0, 15, and 30 min in deionized (DI) water, and corresponding images of leaching ZnO nanoparticles were captured.

3. RESULTS AND DISCUSSIONS

The schematic diagram of the synthesis process for ZnO-based nanoparticles over the textile fabric is illustrated in Figure 1. The enlarged view of the high-resolution SEM micrograph confirms the uniform and dense growth of ZnO particles over a single cotton fiber.

Figure 2 shows the XRD pattern of pristine and irradiated ZnO nanoparticles at various exposure doses. XRD results revealed that the synthesized ZnO nanostructure has a polycrystalline hexagonal wurtzite structure as the values of 2θ = 31.68, 34.30, and 36.17° correspond to (100), (002), and (101) diffraction peaks, respectively. Based on the comparison of XRD peak intensities, it can be clearly seen that the integrated intensities of the irradiated samples get lower, which confirms the decrease in the ordering and crystallinity of the nanostructure. After exposing to a higher dose of gamma ray irradiation, the degradation of the integrated intensity lies around 59.6%, which is attributed to the defects created in the ZnO nanostructure. The grain sizes of the ZnO nanoparticles before and after irradiation have been calculated using Scherrer’s formula

\[ D = \frac{K \lambda}{B \cos \theta} \]

where K denotes Scherrer’s constant, which is equal to 0.9; \( \lambda \) is the wavelength of the X-ray of Cu Kα radiation = 1.5406 Å; B is the full width at half maximum (FWHM) in radians of respective peaks; and \( \theta \) is Bragg’s diffraction angle. Table 1 shows the average crystallite size of ZnO nanoparticles. Only (101) peaks are reported in Table 1; nevertheless, the integrated intensity degradation, peak shift, and deviation in particle size change are quite similar for (100) and (002) peaks. It can also be noticed from Figure 2 that the FWHM values of the samples after irradiation are reduced, which means that the grain sizes of the nanostructure increased. A slight shift of the peak positions to higher angles in comparison with the pristine sample has been found, which could be attributed to strain on the ZnO nanostructures by gamma ray irradiation.

From Table 2, it is interesting to note that the lattice parameters shrink after gamma irradiation, which is consistent with the work of Salari et al. Lattice parameters of the ZnO nanostructure before and after irradiation are calculated as listed in Table 2, which are very similar to the powder diffraction file (PDF 00-036-1451). The decrease in lattice parameters is possible due to the oxygen deficiencies created in the sample or segregated in the form of radicals after gamma ray irradiation. In addition, Goland and Keating had demonstrated that interstitial dislocation loops in the hexagonal structure might lead to an increase in the lattice parameter in the perpendicular direction, and the basal loops produce strain along the c axis. In order to understand the uniformity and the morphology of the film, FE-SEM has been performed as shown in Figure 3. No noticeable change from the surface morphology and the physical appearance (Figure S1) can be observed in the case of pristine as well as the samples irradiated up to 9 kGy.

The optical absorbance and the energy band gap of pristine and gamma ray-irradiated samples were analyzed using a UV-visible spectrophotometer in the wavelength ranging from 300 to 800 nm, as shown in Figure 4. In order to understand the

| dose      | a (Å) | c (Å) | volume (Å³) |
|-----------|-------|-------|-------------|
| pristine  | 3.266 | 5.22  | 48.21       |
| 1.5 kGy   | 3.252 | 5.216 | 47.77       |
| 9 kGy     | 3.250 | 5.212 | 47.67       |
| PDF-00-036-1451 | 3.249 | 5.206 | 47.62       |

Table 1. XRD Measurement Data of the ZnO (101) Peak

| dose     | degradation of (101) peak intensity (%) | peak position (°) | grain size (nm) |
|----------|----------------------------------------|-------------------|-----------------|
| pristine | 0                                      | 36.18             | 15.94           |
| 1.5 kGy  | 36                                     | 36.21             | 17.36           |
| 9 kGy    | 59.6                                   | 36.24             | 16.14           |

Figure 3. SEM micrograph of ZnO nanoparticle-coated cotton fabrics: (a) bare cotton, (b) ZnO-coated cotton (pristine), (c) 1.5 kGy, and (d) 9 kGy samples.
changes in the optical energy band gap, the Tauc plot method has been plotted in \((ahv)^2\) versus \(hv\), which is shown in the inset of Figure 4. From the Tauc plot method, it is found that the energy band gap shifted from 3.32 to 3.34 eV at higher doses. This increase in the band gap may be due to an increase in the carrier concentration after gamma ray irradiation, resulting in the shifting of the absorption edge toward the UV range. This type of phenomena related to an increase in the band gap can be explained by the Burstein–Moss effect.24–27

The optical band gap is defined as the minimum energy needed to excite an electron from the valence band (VB) to the conduction band (CB), and the Fermi level lies in between the CB and VB.28 As the samples are exposed to irradiation, the number of electrons in the VB and CB are changed due to the defects created, which implies the possibility of intermediate states. As the carrier concentration increases due to the irradiation, the lowest state of the CB is filled by free electrons, which suggests that the possibility of a Fermi level might move toward the CB region. Hence, the valence electrons require extra energy to be excited to higher energy states within the conduction band. This is why the optical band gap gets enhanced after irradiation. A similar effect was found in the Al-doped ZnO in which an additional carrier concentration is gained by Al doping,29 whereas in our case, this energy band gap shift has been obtained due to gamma irradiation. Another possibility is due to the lattice parameter shrinkage after irradiation. The decrease in lattice parameters leads to stronger bonding between valence electrons and ion cores, resulting in a larger energy band gap.

To determine the change in the electronic structure of the particles due to gamma ray irradiations, X-ray absorption studies have been performed. As per the dipole selection rule, the \(L_3\) edge represents the unoccupied s- and d- derived states. As 3d states are occupied in ZnO, the \(L_3\) edge is very sensitive to transitions from 2p to both 4s and 4d unoccupied states.30,31 In Figure 5a, feature A comes from Zn 4 s states, whereas features B and C are dominated by 4d transition states. It is accepted extensively that the relative height of the main peaks in the white line spectra can be related to the existence of vacancies, evidenced by polarization effects in crystalline structures.32 Especially, more attention is paid to feature B since it is the most sensitive to the local deficiency or excess of O in the absorber vicinity. From the near-edge spectra of Zn \(L_3\), it can be seen that there is a pre-edge shift by \(\sim 0.2\) eV to lower energies at higher doses. The increase in features A, B, and C indicates the highest unoccupied outermost valence orbitals for irradiated samples in comparison with the pristine sample, which might be due to oxygen deficiency or loss of Zn valence electrons after gamma ray irradiation. The O–K edge is related to the transitions from 1s to 2p orbitals. In Figure 5b, features A1, A2, and A3 represent the transitions into O 2p states hybridized within 4 s states, whereas features A4 and A5 correspond to the transition of 2p states hybridized with Zn 4p states.33,34 Beyond 550 eV, the transitions are due to the hybridization of O 2p with Zn higher extended states. After irradiation, it can be observed from the O–K edge that the density of states of the irradiated samples gets reduced, which might be attributed to the completely filled valence orbitals in comparison to the pristine sample. The features A1, A2, A3, A4, and A5 give us evidence that the oxygen concentration is higher in pristine samples, whereas after irradiation it decreases due to the oxygen deficiency created in the sample, which is consistent with the Zn \(L_3\) edge. This kind of change in the NEXAFS spectra indicates that the most probable point defects found in this structure are due to oxygen vacancies, but it does not discard the presence of a much lower concentration of antisite oxygen atoms (O\(_{\text{Zn}}\)) in the ZnO structure.35

In order to examine the further changes in the chemical states of the elements before and after irradiation, XPS has been performed. XPS analysis revealed the existence of Zn, O, and C, and no other impurities are found on the surface. Figure 6 shows the Zn 2p XPS spectrum of pristine and irradiated samples. In pristine samples, the peaks at binding energies (B.E.) of 1023 and 1046 eV correspond to the spin orbit of Zn 2p\(1/2\) and Zn 2p\(3/2\), respectively.36 The splitting of the 2p doublet is around 23 eV, indicating the presence of Zn\(^{2+}\) in the ZnO films.37 However, a shift in the B.E. of Zn 2p peaks by 2 eV at 1.5 kGy and by 4 eV at 9 kGy toward higher energies with respect to the pristine sample. This B.E. shift toward higher energies after irradiation may be attributed to the decrease in valence electron density and an increase in the oxidation state.38 In a previous work, Yamuna et al. have noted that ZnO-containing boron nitride carbon sheets resulted in a...
shift of B.E. of around 5.4 eV (i.e., at 1027 eV) at 300 °C; however, annealing at 500 °C resulted in the large shift of B.E. to 1021.6 eV due to the removal of NOx, oxygen, and other intermediate products formed during the formation of ZnO hybrid boron nitride structures.39 Yet, compared to Yamuna and co-workers’ work, the necessity of annealing at a high temperature can be replaced by gamma ray exposure to gain higher B.E. In our case, irradiation results in the shift of B.E. up to 4 eV at room temperature only when the ZnO nanoparticle is coated over the cotton fabric. In comparison with the pristine case, this B.E. shift of 2 and 4 eV at 1.5 and 9 kGy, respectively, might be due to the defects created along the bulk ZnO nanoparticles, and the oxygen ions transfer from the surface of ZnO nanoparticle to the radicals formed in the cotton textile fabrics after gamma ray irradiation. Nevertheless, the B.E. shift to more than 2 eV is crucial as the oxidation state of Zn could be attributed to the number of reactions that takes place at the interface of ZnO and the cotton fabric, such as ionization or excitation of the molecules especially on both ZnO and the cotton textile fabric. Drábková et al.40 reported that gamma irradiation on textile fibers might lead to free radical formations. These radicals are highly active; therefore, they are prone to react with compounds like oxygen or water. Further, the radiolysis process can lead to the formation of hydroxyl radicals, which in turn leads to hydrogen peroxide formation, leading to Zn4+ on the surface of ZnO. Lee et al.41 also observed that near the surface, active Zn radicals react with oxygen similar to the treatment of ZnO by H2O2. This resulted in the higher oxidation state of Zn only on the surface, leading to the shift of B.E. to higher values. On the other hand, bulk ZnO is more compact and has less oxygen vacancy in the ZnO structure. This could be the possible scenario for a chemical shift of around 4 eV at higher doses. Moreover, XPS is a surface-sensitive technique, whereas XAS corresponds to a more bulk-sensitive tool for the characterization of materials, thus leading to the variations in the spectra analysis that have been observed. Shettigar’s group has reported earlier that the increase in the carrier concentration results in the increased energy band gap values of the samples after irradiation. This result is consistent with our NEXAFS results, which also suggested the increase in the carrier concentration.27 Overall, this work gives us the insight that gamma ray exposure on ZnO nanoparticles, and the oxygen ions transfer from the surface of ZnO nanoparticles to the radicals formed in the cotton textile fabrics at room temperature rather than being annealed at higher temperatures.

In order to confirm the binding enhancement practically, a stability (washability) test of the ZnO nanoparticles on the cotton fabrics has been carried out by an ultrasonication process for 30 min in DI water. The color of the water turned whitish after 30 min of sonication for pristine samples as shown in Figure S2, suggesting the adhesion is poor for the pristine sample. However, the higher-dose gamma-irradiated sample reveals less leachability of ZnO nanoparticles, which coincides with the results obtained from XPS, and supports the enhanced linkage existing between ZnO nanoparticles and cotton fabrics.

In addition, we also performed a photocatalytic self-cleaning study on bare cotton, pristine, and irradiated ZnO-coated fabrics with absorbed MB under UV illumination. At 0 min, bare cotton seems to adsorb more MB in comparison with the sample of ZnO-coated fabrics because of different adsorption properties, whereas it can be observed that the photocatalytic self-cleaning of ZnO-coated cotton fabrics with gamma irradiation is better than the nonirradiated sample at 120 min. This further gives us the suggestion that the photocatalytic self-cleaning is higher for irradiated ZnO-coated cotton fabric samples. The detailed result is shown in the Supporting Information, which is shown in Figure S3.

As for the color of ZnO on the cotton system, the color is not changed after 9 kGy irradiation. The hydrophilicity test also shows that the system still remains highly hydrophilic after 9 kGy. Although the mechanical test and antibacterial function have not been done in this work, the previous result obtained by Machnowski et al.42 showed the changes in the tensile strength and elongation of fabrics before and after gamma irradiation up to exposures of 100 kGy dose. Their result revealed that the tensile strength and elongation of fabrics degradation of about 5.8 and 6.1% after a dose of about 10 kGy, respectively, which is small for most of the practical applications. As for the antibacterial function, the ZnO–cotton system has been studied by dd’’Aqua et al.19 which shows a positive result for the antibacterial function. The gamma ray irradiation of this system enhances the linkage between the ZnO nanoparticle and the cotton fabric, which can be more beneficial to the application.

In summary, this work further suggests that gamma ray exposure results in an enhancement of binding between the nanoparticle and cotton fabric, which in turn can be served as an important functional material in the textile industry.

4. CONCLUSIONS

Gamma-irradiated ZnO-based functional materials over cotton fabrics were studied to reveal the change in the crystallinity, chemical and electronic properties, and the enhancement of linkage between the ZnO nanoparticle and cotton fabric after gamma ray irradiation. XRD studies revealed the decrease in crystallinity, reducing to almost 59.6% after exposure to 9 kGy, whereas SEM does not reveal any significant change in the surface morphology. XRD results also revealed shrinkage in lattice parameters of ZnO particles after irradiation and become more compact in comparison with the pristine one. The gradual decrease in the XRD integrated intensity and lattice parameters could be due to the oxygen deficiency or defects created in the sample after gamma ray exposure. An increase in the dose level leads to the increased optical band gap energy, which may be attributed to the decrease in lattice parameters, owing to oxygen deficiency in the ZnO nanostructure after irradiation. Moreover, these results are consistent with NEXAFS results obtained from the Zn L3 edge and O-K edge, suggesting the possibility of oxygen deficiency created in the samples after irradiation. However, the results from NEXAFS and XPS are contradictory with each other due to the fact that the former is bulk sensitive and the latter is surface sensitive. In the case of XPS spectra, the B.E. shift by 2 eV at 1.5 kGy to 4 eV at 9 kGy in comparison with the pristine sample. This observed phenomenon of B.E. shift by more than 2 eV in this kind of ZnO-based system is totally different from other reported works. Such a difference might be due to the defects created in the surface of ZnO particles after gamma ray exposure. It could be due to oxygen ions that transfer from the surface of Zn nanoparticles to the radical formation on the surface of cotton fabrics after gamma ray irradiation. Overall, this work suggests that it could be exploited for enhancing the
binding between the coated functional nanoparticles with cotton fabrics, which can be served as an alternative approach for the functional cloth in the textile industry.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01050.

Physical appearance of ZnO nanoparticles coated over fabrics; washability of the ZnO nanoparticles on the cotton fabric; and self-cleaning of bare cotton, pristine and irradiated ZnO coated cotton fabrics (PDF)

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Notes

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**REFERENCES**

(1) Wang, Y.-W.; Shen, R.; Wang, Q.; Vasquez, Y. ZnO Microstructures as Flame-Retardant Coatings on Cotton Fabrics. *ACS Omega* 2018, 3, 6330–6338.

(2) Kołodziejczak-Radzimska, A.; Jesionowski, T. Zinc Oxide-From Synthesis to Application: A Review. *Materials* 2014, 7, 2833–2881.

(3) Ward, K. *Chemistry and chemical technology of cotton*; Interscience Publishers: New York, 1955; p 782.

(4) Riaz, S.; Ashraf, M.; Hussain, T.; Hussain, M. T.; Rehman, A.; javid, A.; Iqbal, K.; Baiz, A.; Aziz, H. Functional finishing and coloration of textiles with nanomaterials. *Color. Technol. 2018*, 134, 327–346.

(5) Wang, J.; Zhao, J.; Sun, L.; Wang, X. A review on the application of photocatalytic materials on textiles. *Text. Res. J.* 2014, 85, 1104–1118.

(6) Verbic, A.; Gorjanc, M.; Simončič, B. Zinc Oxide for Functional Textile Coatings: Recent Advances. *Coatings* 2019, 9, 550.

(7) Gupta, S.; Chang, C.; Anbalagan, A. K.; Lee, C.-H.; Tai, N.-H. Reduced graphene oxide/zinc oxide coated wearable electrically conductive cotton textile for high microwave absorption. *Comp. Sci. Technol. 2020*, 188, 107994.

(8) Moon, Y.-K.; Moon, D.-Y.; Lee, S.; Park, J.-W. Enhancement of ZnO thin film transistor performance by high-dose proton irradiation. *Nucl. Instrum. Methods Phys. Res., Sect. B* 2010, 268, 2522–2526.

(9) Fraboni, B.; Cavallini, A.; Auricchio, N.; Bianconi, M. Deep traps induced by 700 keV protons in CdTe and CdZnTe detectors. *IEEE Trans. Nucl. Sci.* 2007, 54, 828–833.

(10) Kang, R.; Noh, Y.-J.; Yun, J.-M.; Kim, H.; Myoung, N.; Lee, E.-H.; Kim, T.-W.; Na, S.-I.; Oh, S.-H. ZnO films using a precursor solution irradiated with an electron beam as the cathode interfacial layer in inverted polymer solar cells. *RSC Adv.* 2017, 7, 26689–26696.

(11) Güür, E.; Coşkun, C.; Tüzemen, S. High energy electron irradiation effects on electrical properties of Au/n-ZnO Schottky diodes. *J. Phys. D: Appl. Phys.* 2008, 41, 105301.

(12) Turos, A.; Jóźwik, P.; Wójcik, M.; Gaca, J.; Ratajczak, R.; Stonert, A. Mechanism of damage buildup in ion bombarded ZnO. *Acta Mater.* 2017, 134, 249–256.

(13) Reyhani, A.; Gholizadeh, A.; Vaheidi, V.; Khanlary, M. R. Effect of gamma radiation on the optical and structural properties of ZnO nanowires with various diameters. *Opt. Mater.* 2018, 75, 236–242.

(14) Yasaka, P.; Pattanaboonme, N.; Kim, H. J.; Limkitjaroenporn, P.; Kaewkho, J. Gamma radiation shielding and optical properties measurements of zinc bismuth borate glasses. *Ann. Nucl. Energy* 2014, 68, 1–9.

(15) Alarcón, J.; Poncio, S.; Paraguay-Delgado, F.; Rodríguez, J. Effect of γ-irradiation on the growth of ZnO nanorod films for photocatalytic disinfection of contaminated water. *J. Colloid Interface Sci.* 2011, 364, 49–55.

(16) Azmy, N. A. A.; Abdullah, H.; Naim, N. M.; Hamid, A. A.; Shaari, S.; Mokhtar, W. H. M. W. Gamma irradiation effect on the structural, morphology and electrical properties of ZnO-CuO doped PVA nanocomposite thin films for Escherichia coli sensor. *Radiat. Phys. Chem.* 2014, 103, 108–113.

(17) Baydogan, N.; Özdemir, 0.; Cimenoglu, H. The improvement in the electrical properties of nanopherical ZnO:Al thin film exposed to irradiation using a Co-60 radioisotope. *Radiat. Phys. Chem.* 2013, 89, 20–27.

(18) Jaber, B.; Lañah, L. One step synthesis of ZnO nanoparticles in free organic medium: Structural and optical characterizations. *Mater. Sci. Semicond. Process.* 2014, 27, 446–451.

(19) d’Agua, R. B.; Branquinho, R.; Duarte, M. P.; Maurício, E.; Fernando, A. L.; Martins, R.; Fortunato, E. Efficient coverage of ZnO nanoparticles on cotton fibres for antibacterial finishing using a rapid and low cost in situ synthesis. *New J. Chem.* 2018, 42, 1052–1060.

(20) Sarangi, S. N. Controllable growth of ZnO nanorods via electrodeposition technique: towards UV photo-detection. *J. Phys. D: Appl. Phys.* 2016, 49, 355103.

(21) Salari, M. A.; Sağlam, M.; Güzeldir, B. The protection from the effects of gamma rays of metal-semiconductor diodes by means of ZnO thin interface layer. *Radiat. Phys. Chem.* 2019, 165, 108416.

(22) Li, X.; Wang, Y.; Liu, W.; Jiang, G.; Zhu, C. Study of oxygen vacancies’ influence on the lattice parameter in ZnO thin film. *Mater. Lett.* 2012, 85, 25–28.
(23) Goland, A. N.; Keating, D. T. Lattice parameter, volume and length changes in crystals containing dislocation loops. J. Appl. Phys. 1970, 41, 814.

(24) Bhat, J. S.; Patil, A. S.; Swami, N.; Mulimani, B. G.; Gayathri, B. R.; Deshpande, N. G.; Kim, G. H.; Seo, M. S.; Lee, Y. P. Electron irradiation effects on electrical and optical properties of sol-gel prepared ZnO films. J. Appl. Phys. 2010, 108, No. 043513.

(25) Jo, Y. J.; Hong, C. H.; Kwak, J. S. Improved electrical and optical properties of ITO thin films by using electron beam irradiation and their application to UV-LED as highly transparent p-type electrodes. Curr. Appl. Phys. 2011, 11, S143–S146.

(26) Nisha, M.; Anusha, S.; Antony, A.; Manoj, R.; Jayaraj, M. K. Effect of substrate temperature on the growth of ITO thin films. Appl. Surf. Sci. 2005, 252, 1430–1435.

(27) Shettigar, N.; Pramodini, S.; Kityk, I. V.; Abd-Leffil, M.; Eljald, E. M.; Beqragui, M.; Antony, A.; Rao, A.; Sanjeev, G.; Ajeyakashi, K. C.; Poornesh, P. Tuning the third-order nonlinear optical properties of In:ZnO thin films by 8 MeV electron beam irradiation. J. Phys. Chem. Solids 2017, 110, 260–265.

(28) Sernelius, B. E.; Berggren, K.-F.; Jin, Z.-C.; Hamberg, I.; Grandqvist, C. G. Band-gap tailoring of ZnO by means of heavy Al doping. Phys. Rev. B 1988, 37, 10244–10248.

(29) Raghu, P.; Srinatha, N.; Naveen, C. S.; Mahesh, H. M.; Angadi, B. Investigation on the effect of Al concentration on the structural, optical and electrical properties of spin coated Al:ZnO thin films. J. Alloys Compd. 2017, 694, 68–75.

(30) Chen, C.-Y.; Lai, K.-Y.; Lo, J.-W.; Lin, C.-A.; Chiu, S.-H.; Chao, Y.-C.; He, J.-H. Electronic Structures of Well-Aligned Er-Doped ZnO Nanorod Arrays. J. Nanosci. Nanotechnol. 2011, 11, 10615–10619.

(31) Mosquera, A. A.; Horwat, D.; Rashkovskiy, A.; Kovalev, A.; Miska, P.; Wainstein, D.; Albella, J. M.; Endrino, J. L. Exciton and core-level electron confinement effects in transparent ZnO thin films. Sci. Rep. 2013, 3, 1714.

(32) Haug, J.; Chassé, A.; Dubiel, M.; Eisenschmidt, C.; Khalid, M.; Esquínazi, P. Characterization of lattice defects by x-ray absorption spectroscopy at the Zn K-edge in ferromagnetic, pure ZnO films. J. Appl. Phys. 2011, 110, No. 063507.

(33) Dong, C. L.; Persson, C.; Vayssieres, L.; Augustsson, A.; Schmitt, T.; Mattesini, M.; Ahuja, R.; Chang, C. L.; Guo, J. H. Electronic structure of nanostuctured ZnO from x-ray absorption and emission spectroscopy and the local density approximation. Phys. Rev. B 2004, 70, 195325.

(34) Devi, V.; Kumar, M.; Shukla, D. K.; Choudhary, R. J.; Phase, D. M.; Kumar, R.; Joshi, B. C. Structural, optical and electronic structure studies of Al doped ZnO thin films. Superlattices Microstruct. 2015, 83, 431–438.

(35) Gallach, D.; Muñoz-Noval, A.; Torres-Costa, V.; Manso-Silván, M. Luminescence and fine structure correlation in ZnO permeated porous silicon nanocomposites. Phys. Chem. Chem. Phys. 2015, 17, 20597–20604.

(36) Sankar ganes, R.; Navaneethan, M.; Mani, G. K.; Ponnumamy, S.; Tsuchiya, K.; Muthamizhchelvan, C.; Kawasaki, S.; Hayakawa, Y. Influence of Al doping on the structural, morphological, optical, and gas sensing properties of ZnO nanorods. J. Alloys Compd. 2017, 698, 555–564.

(37) Ranjith, K. S.; Nivedita, L. R.; Asokan, K.; Krishnamurthy, S.; Pandian, R.; Kamrardin, M.; Avasti, D. K.; Kumar, R. T. R. Robust water repellent ZnO nanorod array by Swift Heavy Ion Irradiation: Effect of Electronic Excitation Induced Local Chemical State Modification. Sci. Rep. 2017, 7, 3251.

(38) Nakamura, A.; Temmyo, J. Schottky contact on ZnO nanocolumnar film with H2O2 treatment. J. Appl. Phys. 2011, 109, No. 093517.

(39) Yamuna, A.; Mandalam, A.; Karthigaiselvi, A.; Balasubramanian, M.; Thiruparasakthi, B.; Ravichandran, S.; Mayavan, S. One-step synthesis of boron nitride carbon nanosheets containing zinc oxide for catalysis of the oxygen reduction reaction and degradation of organic dyes. RSC Adv. 2015, 5, 69394–69399.

(40) Drábková, K.; Šurowič, M.; Kučerová, I. Influence of gamma radiation on properties of paper and textile fibres during disinfection. Radiat. Phys. Chem. 2018, 152, 75–80.

(41) Lee, H.-Y.; Wu, B.-K.; Chen, M.-Y. Study on the Formation of Zinc Peroxide on Zinc Oxide with Hydrogen Peroxide Treatment Using X-ray Photoelectron Spectroscopy (XPS). Electron. Mater. Lett. 2014, 10, 51–55.

(42) Machnowski, W.; Gutarowska, B.; Perkowski, J.; Wrzosek, H. Effects of gamma radiation on the mechanical properties of and susceptibility to biodegradation of natural fibers. Text. Res. J. 2012, 83, 44–55.