Effect of γ-ray irradiation on the physical properties of PANI/TiO_2 nanocomposite thin films

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Abstract: In this paper the effect of γ-ray irradiation on PANI/TiO_2 nanocomposite thin films was investigated and the prepared thin films for used as dosimeters. The morphology and structural properties of PANI/TiO_2 nanocomposite thin films as well as their electrical conductivity and optical absorption were examined before and after the influence of γ-ray irradiation on them. Samples were synthesized by a chemical oxidative polymerization method. The PANI/TiO_2 nanocomposite thin films were exposed to a (Cs^{137}) γ-radiation source at different dose 0, 2, 6, and 8 kGy in room temperature. The morphology of the PANI/TiO_2 nanocomposite thin films was studied using field emission scanning electron microscopes (FS-SEM). The X-ray diffraction analysis shows that the impact of γ-ray irradiation on the structure phase state of samples. The study of electrical conductivity (σ) illustrates that the unirradiated PANI/TiO_2 nanocomposite thin films have conductivity 3.13 S/cm and increase to 5.91S/cm after exposed to 8 kGy dose γ-ray irradiation. Absorption spectra for PANI/TiO_2 nanocomposite thin films were recorded and their analysis demonstrates that the radiation doses of gamma rays lead to increase the absorbance. The observed changes in the physical properties suggest that PANI/TiO_2 nanocomposite thin films can be used as an effective material for gamma-radiation dosimeters at room temperature.
Keyword: Conductive Polymer, PANI/TiO_2, Gamma irradiation, Thin films

Introduction

Improvements in the conductive polymer thin films on a nanometer scale have received significant attention in recent years due to a wide range of potential applications in opto-electronic devices. Conductive polymer nano-composites are expected to have modified electrical, optical and structural properties. A new generation of synthetic metals has been tested for the unique combination of electrical and optical properties of conductive polymers. The synthesis of the conductive polymers was achieved by oxidizing or reducing by chemical or electrochemical doping. Due to its relative ease of preparation, excellent environmental stability and tunable conductivity, polyaniline (PANI) is the most studied polymer [1].

Polymer nano-composites are electrically-conductive polymer composites and use various types of nanoparticles to enhancement the electrically properties of polymer. The polymer matrix has the following advantages: excellent resistance to chemical, low costs, low density, oxidation and high processability. Nano-particles have characteristics, including interfaces and large surface, nano-composite magnet permeability and electrical conductivity. The nanoparticles widely castoff include metal oxides, metal nanostructures, semiconductor and carbon materials [2].

Nanocomposite materials grounded on inorganic nanostructures & organic polymers; it have been at the vanguard of research & development. A number of compounds, including the hybrids of carbon nanostructures, metal nanoparticles, and metal chalcogenides, have been introduced (in detail quantum dots with CPs). Hence the oxide semi-conductors of the appropriate content and with a broad variety of properties can be coupled with organic counterpart complementary characteristics [3, 4].

In the presence of TiO_2 particles, PANI/TiO_2 nanocomposites can be achieved by in situ chemical aniline oxidation. Generally, aniline oxidation can produce a variety of products, such as oligomers and oxidation products with an ortho-position amino group [5].

Polymer irradiation has proven to be among the most acceptable methods of changing the structure of polymers significantly. Polymer irradiation changes the initial structure by cross-linking, irreversible bonding and free radical formation, creation of saturated and unsaturated classes and leading to molecular fragmentation. All of these methods familiarize so-called defects within the material responsible for the alters the mechanical, optical, chemical and electrical properties of the polymers [6,7,8].

In this study, PANI/TiO_2 nanocomposite thin film was produced using in-situ polymerization method and subsequently irradiated with different doses of gamma rays. The influence of radiation on morphological characteristics, structure, electrical and optical properties and the feasible use of PANI/TiO_2 nanocomposite thin film as gamma dosimeters have been investigated.

Experimental setup

The PANI/TiO_2 nanocomposite thin films were chemically synthesized by in-situ polymerization method, where using aniline monomer and ammonium persulfate (APS) as oxidant agent and hydrochloric acid (HCL) as protonic acid dopant, accordance to a method similar to the described by Tariq J. and Zian M. 2020 [9]. The 3 Wt% of TiO_2 nanoparticles mixed with aniline were used. PANI/TiO_2 nanocomposite thin films were deposited on glass slides. The slides were dipped in aniline/TiO_2/HCl solution, then the oxidant agent (APS) was added under constant stirring to start the polymerization process, after 30 min, all the slides are removed from a baker, then rinsed acetone, finally left to dry in air at room temperature. The samples were irradiated by gamma rays at various doses 0, 2, 4, 6 and 8 kGy, at room temperature by using Cs^{137} as a gamma source. Infrared analysis at a wave number range of 600–4000 cm^{-1} was conducted using a SIDCO England series FT-IR spectrometer. The morphological characteristics and surface topography of the films were imaged using field emission scanning electron microscopes. The structure of these samples was investigated by using Philips X-ray diffraction (XRD) diffractometers. The optical measurements of the PANI/TiO_2 nanocomposite thin films were performed on the basis absorbance spectra at 300-900 nm by using a UV-VIS spectrophotometer type SHIMADZU UV-VIS 1600/1700 series.

Results and discussions

The morphologies of the PANI/TiO_2 nanocomposite thin films and γ-PANI/TiO_2 nanocomposite thin films were analyzed by FS-SEM. As shown in Fig. 1, PANI/TiO_2 and γ-PANI/TiO_2 thin films exhibit similar morphologies features, the inspection of the image of PANI/TiO_2 as shown in figure 1 reveals that it contains structure like a nano-rods structure with unsmooth surfaces of these nano-rods, and diameters sizes about 191–233 nm, the surface shapes of nano-rods for PANI/TiO_2 and γ-PANI/TiO_2 thin films do not differ much except that the slightly change after irradiation in their diameters which increase from 191 nm to 233 nm after irradiation. Furthermore, FE-SEM images of PANI/TiO_2 and various γ-

PANI/TiO_2 confirm that gamma-ray irradiation have a few influence on the morphology of the PANI/TiO, and this analogous to those reported by other researchers [10,11].

Figure 2. shows the X-ray diffraction patterns of the PANI/TiO_2 and γ-PANI/TiO_2 nanocomposite thin films, measured in the 2θ range 10°–80°. The characteristic patterns for the non-irradiated PANI/TiO_2 nanocomposite thin films indicates that they have amorphous phase with the broad faint reflection at 2 θ =25°, while the γ-PANI/TiO_2 nanocomposite thin films have shown two peaks in the 2θ at 25°, 48°, due to the transform to semicrystalline phase as a result of the gamma effect. The integral intensity (I) vs. the gamma dose shown in Figure 3, the I shows a rise with increasing the gamma dose. this is often attributed to a rise within the crystallinity, which represents the improvement in crystallinity. This may result from cross-linking of the polymer chain or the creation of single or multiple helices, which leads to form more crystalline regions in the polymer samples [12,13].

Polyaniline polymers synthesized by chemical method, can have σ between 10^{-10} and 1 S/cm. The σ of polyaniline depends on its oxidation state and degree of protonation [14,15].

The graph of σ versus gamma dose for all samples presents in Figure 4, the average conductivity of PANI/TiO_2 and γ-PANI/TiO_2 nanocomposite thin films at higher irradiation doses 8 kGy are about 3.13 S/cm and 5.91 S/cm respectively. The conductivity increase can be caused by the creation of polarons at the defect site, which moves towards the polymer backbone. This means that the degradation due to radiation becomes efficient and thereby increases the free mobility of radicals, which increases the conductivity. The increased conductivity following irradiation is also confirmed by a crystallinity rise as stated previously [12-13].

A Fourier transform IR spectra of the the PANI/TiO_2 and γ-PANI/TiO_2 nanocomposite thin films are shown in Figure 5. It is clearly seen from Figure 5 for PANI/TiO_2 nanocomposite thin films that the bands at at 3346, 1612, 1494, 1259, 1037and 846 cm^{-1} are corresponding to polyaniline [16,17,18]. Characteristic bands for functional groups are shown in Table 1.

For γ- PANI/TiO_2 nanocomposite thin film samples, the only difference in the specific functional group is their strength values, indicating to formation of a new small band for γ-irradiated at 822 and 815 cm^{-1}, respectively. The new band formation indicates a cross-link after irradiation. However, in general, the characteristic bands and their pre-irradiation arrangements were similar to those after irradiation, suggesting that the irradiation did not affect the chemical bonds of PANI/TiO_2 nanocomposite thin film [19,20].

The UV-Vis spectrum of PANI/TiO_2 and γ-PANI/TiO_2 nanocomposite thin films are shown in Figure 6. It is clear from the spectra that the absorbance edge is shifted towards a higher wavelength after irradiation, indicating a reduced in the band gap, thereby increasing conductivity as a result of irradiation. This is due to the improvement of unsaturated conjugate bonds in PANI/TiO_2 after irradiation. In the range of wavelengths studied, it was found that the absorbance in the aromatic compound was due to the π-π* transition [21]. It was also noticed that with the radiation doses of gamma rays, absorption grows, as is clear from the spectra. Transitions occurred between 320-820 nm are attributed to polaron/bipolaron transitions that are prevalent in PANI/TiO_2 nanocomposite thin films [20, 22].

Conclusions

PANI/TiO_2 nanocomposite thin films can be successfully prepared chemically by in-situ polymerization method. Different doses of gamma radiation improve the structural, optical, and electrical properties of the thin films by increasing the crystalline, electrical conductivity, and optical absorbance of the prepared thin films, but such doses have little effect on the morphological characteristics of the prepared thin films. Our results indicate that A PANI/TiO_2 nanocomposite thin films may be used as a material for measuring specific gamma radiation doses of 0, 2, 4, and 8 kGy at room temperature.

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Table (1) The functional groups of PANI/TiO_2 nanocomposite.

Bond type	Wave number cm^{-1}
C–H	846
N–H stretching vibration	3346
N–B–N	1494
N= Q=N	1612

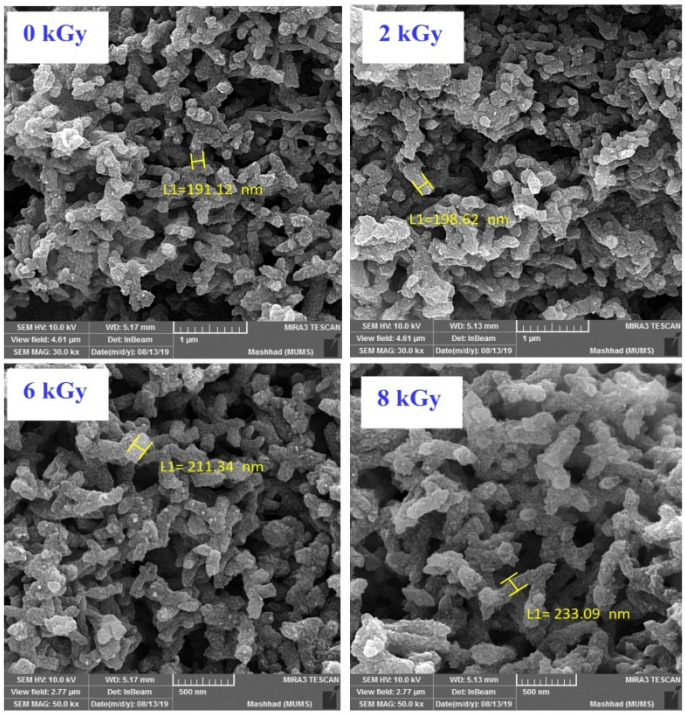

Figure 1. The FE-SEM images of PANI/TiO_2 and various γ-PANI/TiO_2 samples irradiated with different doses of gamma-ray.

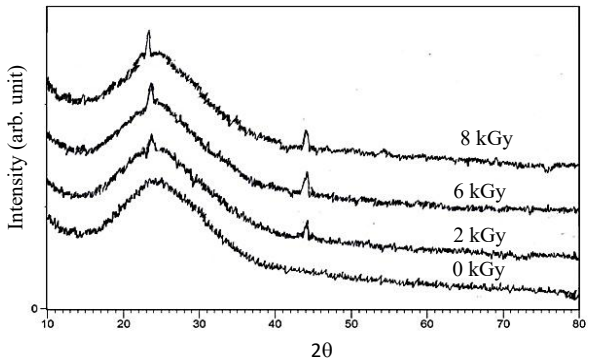

Figure 2. The X-ray diffraction of PANI/TiO_2 and various γ-PANI/TiO_2 samples irradiated with different doses of gamma-ray.

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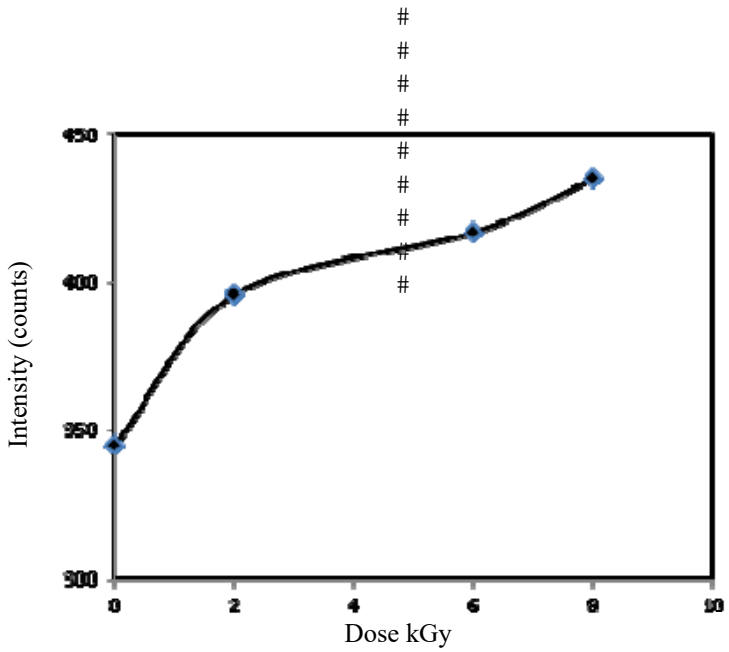

Figure 3. Variation of gamma radiation dose versus integral intensity for PANI/TiO_2 and various γ-PANI/TiO_2 nanocomposite thin films.

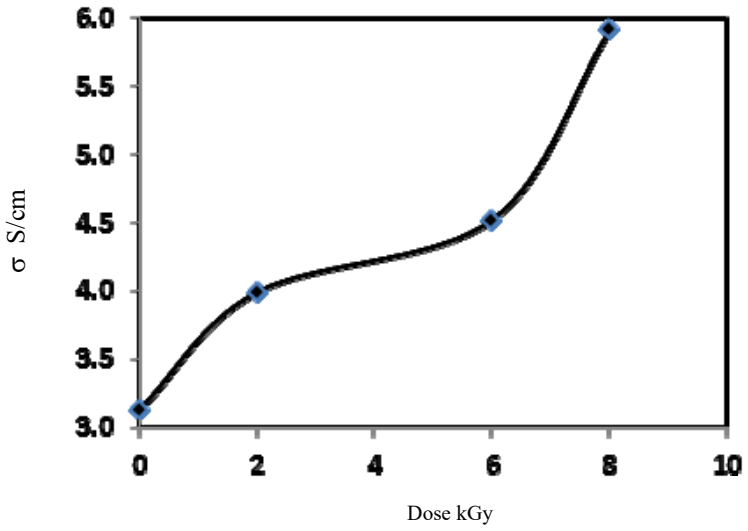

Figure 4. Variation of gamma radiation dose versus electrical conductivities for PANI/TiO_2 and various γ-PANI/TiO_2 nanocomposite thin films.

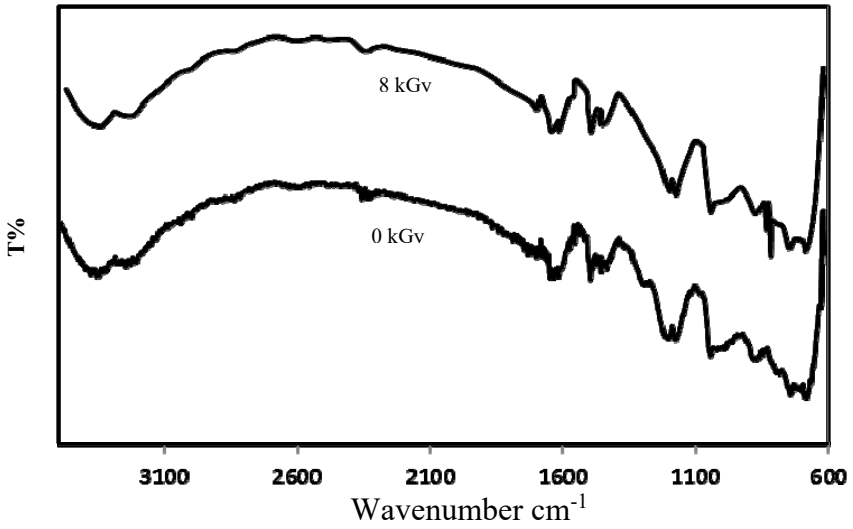

Figure 5. FTIR spectra of the PANI/TiO_2 nanocomposite thin films before and after gamma irradiation.

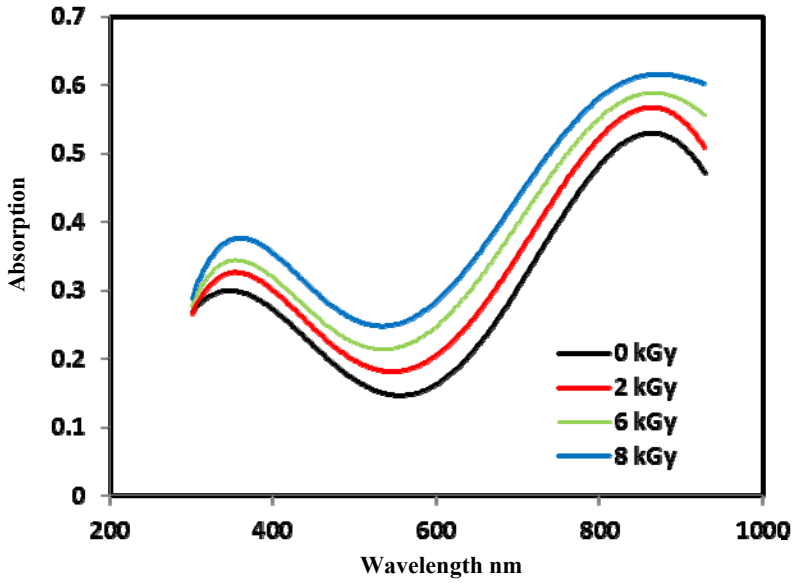

Figure 6. The variation of absorption spectra with wavelength for PANI/TiO_2 and various γ-PANI/TiO_2 nanocomposite thin films.