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1,2-Dihydroxyanthraquinone: Synthesis, and induced changes in the structural and optical properties of the nanostructured thin films due to γ-irradiation

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ABSTRACT

1,2 Dihydroxyanthraquinone (Alizarin-AZ) is available, low-cost organic compound. Besides, AZ has multiple applications owing to its drawing attention photoactivity. This paper is devoted to study the influence of Gamma irradiation on the morphology, optical, and dielectric properties of AZ nanostructured thin films. Nanostructure powder of Alizarin is synthesized according to chemical routes. Subsequently, thin films of AZ are fabricated via thermal evaporator. The bared thin film is irradiated at different doses of ^{60}Co γ-rays. Furthermore, the bared and irradiated films are characterized via X-ray diffraction (XRD), atomic force microscope (AFM) and UV–Vis-NIR spectroscopy. XRD investigations reveal that the bared film has a nanostructure and the average particle size increases gradually as the γ-irradiation dose increases. AFM images show remarkable increment in the surface roughness of the irradiated film over the bared one. In the light of structure induced changes, clear variations in the optical properties are addressed. Of these, the energy gap decreases gradually as the irradiation dose increases. The film irradiated at 45 kGy shows the highest optical conductivity. Based on our results we suggest AZ nanostructured thin films as potential candidate for optoelectronics devices.

1. Introduction

AZ is a natural dye comes from roots of the madder plant [1]. It is chemically known as 1,2 Dihydroxyanthraquinone, and it is prepared for the first time by the ingenious chemist Graebe in 1868 [2]. Usages of AZ come back to Ancient Egyptians, Romans, and Greeks ages where they used it in arts and crafts. Moreover, it is used as well as in the production of fabrics for uniforms and other wear [1].

Recently, usages of AZ are varied and expanded [3–6]. AZ can easily form complexes with metallic ions. Therefore, it is used in monitoring and observing of the trace metals [7]. For example, it is employed on plasmonic Au NPs to detect heavy metals in drinking water and the obtained results of Surface-enhanced Raman spectroscopy revealed the high sensitivity of AZ for cadmium detection from the studied samples [7]. In another context, AZ bright color, low costs, availability, high molar extinction coefficient, strong absorption bands, photo-stability and structure flexibility are seductive properties [6] that encouraged researcher to explore the possibility of introducing AZ as an active absorbing layer in optoelectronic devices. Photo-responsive has been examined using AZ as a donor layer in organic/inorganic hybrid structure device (ITO/AZ: ZnO/Ag) [8]. Under illumination conditions, the device shows a short circuit current (Jsc = 0.034 mA/cm^2), open voltage circuit voltage (V_{oc} = 1.2 V), fill factor (FF = 0.56) and power conversion efficiency (η = 1.2%).

In the field of thin films, the post-treatment processes using highly energetic ionizing radiations such as γ-radiation have been widely explored to enhance the microstructural [9–11], optical [12–14], and electrical [15–17] properties of the materials under investigations. In a relation, AZ pigment is exposed to a high dose of X-ray irradiations (~1.2×10^{17} to ~3.4×10^{-17} photons cm^{-2}) and it does not show any kind of chemical modification [18]. On the contrary, upon exposure to air pollutants such as NO_2 and SO_2 remarkable chemical changes have been detected in AZ [18].

According to the literature [19–21], the most stable sate for AZ molecule originates due to the intramolecular hydrogen-bonded form. In addition, when AZ molecules are excited, the molecule geometry may change due to $\pi \rightarrow \pi^*$ transition of the proton transfer from the OH to the carbonyl oxygen [3]. On the same approach, this paper aims to explore the induced changes in the morphology of AZ thin films before and after exposure to high energy source like ^{60}Co gamma rays with different doses and correlate these changes to the optical properties. The

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reported changes in the refractive index, energy gap and optical conductivity propose AZ nanostructured thin films as potential candidate for photovoltaic devices.

2. Experimental

2.1. Materials

Anthraquinone ($C_{14}H_8O_2$), Sodium perchlorate monohydrate ($NaClO_4 \cdot H_2O$), Potassium hydroxide (KOH), and Sodium hydroxide (NaOH) were purchased from Sigma-Aldrich.

2.2. Alizarin Synthesis

Alizarin nanoparticles (AZ NPs) were synthesized as following: A mixture consists of 50 g Anthraquinone, 15 g Sodium perchlorate monohydrate, 150 g Potassium hydroxide and 50 ml of water was heated at 200 °C for 3 h. Thereafter, the obtained melt was let cool to room temperature and then was dissolved in 300 ml of water. To avoid formation of more precipitate through the solution, air was purged then an overabundance of lime and water were added. The produced calcium salt of alizarin was filtered, suspended in water and it was disintegrated by heating with hydrochloric acid. Subsequently, the hot solution was filtered and the precipitate was dissolved in 15% of sodium hydroxide solution. Moreover, the filtrate was heated to boiling and alizarin was precipitated by adding hot dilute sulfuric acid (1:1). Finally, the mixture was refluxed for 1 h, filtered and washed with hot water to remove sulfuric acid. The obtained powder was distinctive orangish-red color.

2.3. Methods

The chemical structure of the synthesized AZ powder has been identified and confirmed via Fourier-transform infrared spectroscopy (FTIR 3600 infrared spectrometer (Jasco, USA) using KBr as a window material) [22] and depicted in Fig. 1. The functional groups of AZ are previously identified elsewhere [23–26]. Further, the structures of the bared and irradiated films (which were hosted by glass substrates) were checked via conducting X-ray diffraction (XRD; Shimadzu XRD-6000, Japan). XRD patterns were obtained in the range of 2θ from 4° to 90° at room temperature. Cu Kα was used as a radiation source of wavelength λ = 0.15408 nm, scan rate 2°/min, and operation voltage and current are 50 kV and 40 mA, respectively [27]. Thereafter, for optical properties investigations nanostructured AZ thin films have been efficiently fabricated using thermal evaporator (Edwards Co., England, model E 306 A) [28] on quartz substrates. The as-deposited thin films have encountered different doses (0, 15, 30, 45 kGy) of ^{60}Co gamma irradiation. Additionally, the surfaces of the AZ bared film and the film that is irradiated at 45 kGy were scanned via the Atomic Force Microscope (Model: Wet-SPM, Scanning Probe microscope, Shimadzu, Contact mode, Japan) [29]. Furthermore, the UV-Vis-NIR spectroscopy (Shimadzu UV-2101, Japan) was employed to measure the reflectance R (λ) and the transmittance T (λ) in a wide range of wavelengths from 200 to 2500 nm. Subsequently, T (λ) and R (λ) have been computed based on Murmann's exact equations to calculate the refractive index, the extinction coefficient, and the absorption coefficient via a software program privately developed [22,30].

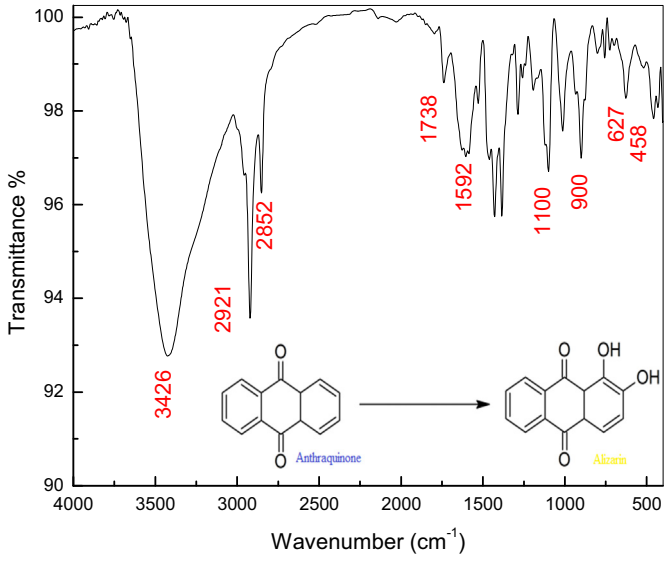

Fig. 1. Molecular structure scheme and FTIR assignments of the dominant bands of the synthesized Alizarin NPs.

3. Theory

The microstructural parameters of nanostructured thin films viz. the average crystallite size, D, the average dislocation density, δ, the microstrain, M, and the particle diameter, d, could be conducted by estimating the broadening width (β) of the most intensive peak and using the following relations [31,32]:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{1}$$

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

$$M = \frac{\beta}{4 \tan\theta} \tag{3}$$

$$d = \frac{\lambda}{\sin(\beta)\cos(2\theta)} \tag{4}$$

where, θ is the diffraction angle and λ is the wavelength of X-ray incident photons.

The refractive index, n, the absorption coefficient, α, and the extinction coefficient, k, of the thin films could be obtained from the direct measured values of the transmission T (λ) and the reflectance R (λ) based on the following relations [33–35]:

$$n = \left(\frac{4R}{(1-R)^2} - k^2\right)^{1/2} + \left(\frac{1+R}{1-R}\right) \tag{5}$$

$$\alpha = \left(\frac{1}{t}\right) \ln\left[\left(\frac{(1-R)^2}{2T}\right) + \left(\left(\frac{(1-R)^4}{4T^2}\right) + R^2\right)^{1/2}\right] \tag{6}$$

$$k = \frac{\alpha\lambda}{4\pi} \tag{7}$$

where, t is the thickness of the thin film.

The value of energy gap and the type of the electronic transitions according to the following relation:

$$\alpha h\nu = B(h\nu - E_g)^q, \tag{8}$$

where $h\nu$ is the photon energy of the incident light, B is a constant, E_g is the energy gap and the exponent q is a constant based on the type of transition. In this context, q = 2 or 3 for indirect allowed and forbidden transitions, respectively. However, q = 1/2 or 3/2 for direct allowed and forbidden transitions, respectively.