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Spectrophotometric calculations of optical linearity and nonlinearity of nanostructured Pyronin Y/FTO optical system for optoelectronic applications

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ABSTRACT

Pyronin Y (PY) is an organic dye with semiconducting behavior which can be ascribed as a novel dye in different aspects of material science and device engineering. Thin films of Pyronin Y were prepared using a low-cost spin coating method deposited on FTO substrate. XRD showed that PY thin film has an amorphous structure with crystalline peaks corresponding only to FTO layer/glass. Transmittance, reflectance, and absorbance are measured for Pyronin Y/FTO of thickness around 200 nm at the normal incident light in the wavelength range 300–2500 nm. PY has an absorption valley in the visible region. Based on the measured transmittance and reflectance, the refractive index *n* of PY/FTO is calculated by using the Fresnel's equations. Dielectric constants, dissipation factor, band gap and optical/electrical conductivity were also determined and analyzed. Plotting of $(\alpha h\nu)^{1/2}$ versus the incident photon energy is giving the values of the band gap. Three optical band gaps are found, the highest one is designed for FTO layer/glass and equals 3.569 eV and the other two band gaps are (1.955 and 1.356 eV) for Pyronin Y/FTO film. For PY films on FTO, the value of band gap (1.955 eV) is described the fundamental band gap and the second band gap (1.356 eV) is described as the trap energy inside the fundamental band gap. The nonlinear optical properties including the third order nonlinear optical susceptibility and nonlinear refractive index of PY/FTO glass were calculated and analyzed by using spectrophotometric data. Hence, Pyronin Y/FTO with a graded band gap have a unique optical constant that useful in multi-device applications for physics and engineering.

1. Introduction

It is well known that the organic materials have wide applications in electronics and optoelectronic devices due to their special properties such as low-cost deposition technique, biodegradable and the nature of molecular structure [1]. Organic thin films have many industrial and engineering applications in electronics, optoelectronics, light emitting diode with different colors, photoconductors, nonlinear optics, quantum information, telecommunications, . . . etc [2]. Pyronin Y compound dye is Xanthene derivative and subgroup of fluorenes. It has widely applied in the cell organelles and the labeling of proteins [3]. This dye has a remarkable sensitivity to the molecular environment [4]. There are many application of Pyronin materials as an organic semiconductor in the electronics devices such as rectifiers, photovoltaic cells and organic light emitting diodes [5,6].

I.S. Yahia et al. studied Pyronin Y in powder form and confirmed the semiconducting behavior of this material using dc electrical conductivity. Also, they studied the dielectric properties as a function of the applied frequencies. Fingerprint function groups were confirmed by using Fourier transformation infrared spectroscopy. Optical band gap of Pyronin Y in powder form was analyzed by Kubelka–Munk theory [7].

The aim of the present work is to prepare PY as a new organic semiconductor dye thin film onto FTO glass by using spin coating method. The structure characterization of PY/FTO thin film optical system has been measured using X-ray diffraction (XRD) and atomic force microscope (AFM). The optical constants, optical band

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gap and dielectric constants of Pyronin Y have been determined. In addition to the linear optics, the non-linear optics have been also studied in details. A comparative study with previously reported data about non-linear optics of other dyes is also reported in this study. Up to our knowledge, there is no any data reported about the optical properties of PY/FTO optical system.

2. Experimental details

2.1. Preparation of PY/FTO thin films

Pyronin Y of high purity and fluorine-doped tin oxide (FTO glass) were brought from Sigma-Aldrich company without any extra purification. The molecular weight of Pyronin Y is 302.79856 g/mol with chemical formula $C_{17}H_{19}ClN_2O$. The molecular and chemical structure of PY is shown in Fig. 1. The Pyronin Y solution was prepared by dissolving 10^{-3} M of PY powder (i.e. 0.061 g) in 20 ml of Ethanol. A magnetic stirrer was used to perform the dissolution process of PY with the solvent. The stock solution of PY was left in dark desk to prevent the light interaction between the PY dye and the light. The FTO glass substrates were cleaned by soap, distilled water, and isopropyl alcohol. Homemade design spin coating device was used for the deposition of PY on FTO glass at 1000 rpm for 30 s.

2.2. Devices and measurements

The Structure properties of Pyronin Y/FTO thin films is measured by means of X-ray diffractometry model: Shimadzu Lab XRD-6000 with *CuK*α (λ = 1.5406 Å). This system was operated at 30 kV and 30 mA. The fitted data of FTO peaks was matched by using pdf-2-2002 library attached to this device.

The structural properties of the Pyronin Y thin film onto FTO were investigated by using atomic force microscope from (Model: Next, NT-MDT, Russia) using non-contact mode. All the obtained data such as surface morphology, grain size, and roughness were obtained by using the attached Next software.

Transmittance *T*(λ), reflectance *R*(λ) and absorbance *abs*(λ) of PY/FTO thin film optical system were measured by using JASCO (UV-VIS-NIR) 570 double beam spectrophotometer in the wavelength of 300–2500 nm at the normal incidence. All the above measurements were done at room temperature. It is important to mention that reflectance was measured by specular reflectance technique by using the aluminum mirror as a reference.

The Pyronin Y thin film thickness was determined by using Alpha-Step IQ Surface Profiler and equals 200 nm.

3. Results and discussion

3.1. Structure characterization of Pyronin Y/FTO nanostructured thin film optical system

The structure characterization of PY/FTO thin film was determined by using the X-ray diffraction (XRD). Fig. 2 illustrates the XRD pattern of Pyronin Y thin film coated FTO substrate. The thin films of dye mostly have an amorphous structure. There is no

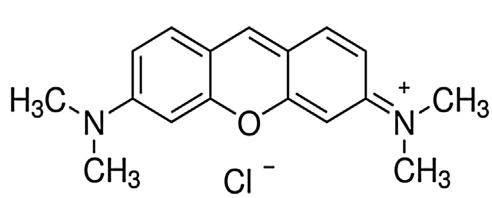

Fig. 1. The molecular structure of Pyronin Y.

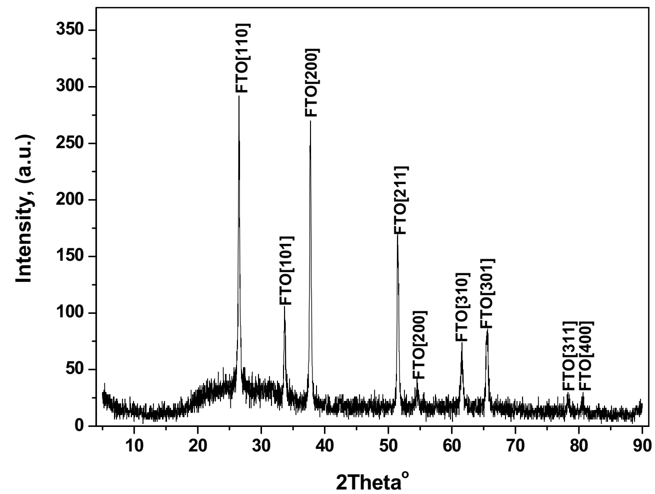

Fig. 2. The X-ray diffraction pattern of Pyronin Y/FTO nanostructured film.

any corresponding peak related to the powder PY [7]. The respective diffraction peaks corresponding to the FTO layer on glass and the unit cells parameter are agreement with the standard FTO that has tetragonal structure and cell parameters as follows: $a = b = 4.7382$Å and c = 3.1871Å and $\alpha = \beta = \gamma = 90^0$. The above data is mentioned in JCDPS (No. 41-1445) for the FTO layer. It is clear that there is no any other peaks represents the pyronin Y layer. From our previous work on organic semiconductors, most of the organic material has an amorphous structure on soda lime and FTO glass substrates [8].

Surface morphology of PY thin film coated FTO substrates was measured by AFM. The 2D/3D patterns of PY/FTO glass substrates are showed in Fig. 3. It is clear that the PY over FTO glass has a uniform structure with spherical morphology. Also, FTO layer can work as a seed for organic materials and it is expected the uniform distributions of PY particles on FTO layer. Both grain size and surface roughness were computed and equal 17.154 nm and 12.345 nm, respectively.

3.2. Optical properties of nanostructured Pyronin Y/FTO thin film optical system

3.2.1. Linear optical properties of nanostructured Pyronin Y/FTO thin film optical system

We measure the optical constants of the PY thin films to determine some optical advantages properties of this material. From studying this optical property, we can determine some parameters useful to design PY device for its applications in optoelectronic and electronic devices. The wavelength dependence of *T*(λ), *R*(λ) and *(abs)* of PY thin films was measured at the wavelength range 300–2600 nm and the thickness 200 nm as shown in Fig. 4. The transmittances curves in Fig. 4 are plotted for both the PY/FTO/glass film as compared to FTO/glass substrate. FTO/glass substrates have a transparency in the visible region up to 81% and then fallen down to zero percent in the far infrared region. Such behavior of FTO layer on glass provides new features of this materials in new technology as follows: high thermal stability, blocking of infrared radiation, highly transparency in the visible region, wide-scale applications in an optoelectronic device, (solar cells, photovoltaics, photodiodes, photo-sensors . . . .etc). Pyronin Y/FTO glass follow the same pattern as a pure FTO/glass substrates, except the production of new absorption valley corresponding to PY only in the wavelength region from 424 nm to 670 nm. Such absorption valley can be described as shoulder like-band. FTO layer limited the transparency of PY layer to be lower than its value. Both