Annals of Agri-Bio Research **27** (2) : 222-226, 2022 **Impact Score : 0.28 (Scopus)**

Influence of Natural Crocus Dye on Morphological and Optical Properties of (PVA/TiO_2) Nanocomposite Prepared by the Spin Coater Method

AMEEN ALWAN MOHAIMEED* AND BAHAA H. RABEE

College of Education for Pure Sciences, Department of Physics, University of Babylon, Iraq
**(e-mail : ameenalwan@87gmial.com; Mobile : 78094 93899)*

(Received : April 30, 2022; Accepted : May 19, 2022)

ABSTRACT

The nanocomposite (PVA/TiO_2/crocus) was prepared and four films were obtained with different concentrations of crocus dye. The results of optical microscopy observed nanoparticles created a continuous network inside polymers. This network had routes that allowed charge carriers to move via them inside the nanocomposites. The vibrational peaks at 3387, 3325.28, 1705.07 and 1080.14/cm were assigned to O–H stretching, C–H stretching, C–H bend of CH_2, C-O and CH rocking of (PVA/TiO2/crocus dye), respectively along with another vibrational peaks for concentrations of nanocomposites. Increased concentration had generated new bonds in this range. Decreasing the FT-IR spectrum in the range of 3387 to 3367.71/cm showed the produced polymer chains which corresponded to O–H stretching and C–H stretching bond. The absorbance for all films had the appearance of a peak at 440 nm, which was due to the crocus dye, and had the greatest transmittance of 81.5 at a concentration of 1 ml, and then it started to decrease. The energy gap decreased from 307eV to 3.58 eV with increased concentration of crocus dye.

Key words : Crocus natural dye, polyvinyl alcohol films/TiO_2 nanoparticles, optical properties, (PVA/TiO_2/crocus dye) nanocomposites, spin coater method, FTIR

INTRODUCTION

The polymers are particles formed by huge numbers of much smaller molecules joining together under the influence of chemical connections (Bahaa and Nasser, 2017). PVA was used in the variety of industries, including manufacturing, commercial, medical and food. Surgical threads, paper goods and food packaging materials have all been made with it. As a result, photovoltaic and optoelectronic devices could use PVA polymers (Alsaad *et al.*, 2021). Natural colouring comes from plants like blackberries, crocuses and many more. Anthocyanin molecules found in these plants absorb light at visible wavelengths, allowing them to absorb photons. Another advantage of utilizing natural dyes as photosensitizers in DSSC was their high visible spectrum absorption coefficients (Maurya *et al.*, 2018). One of the primary components impacting nanocomposite performance was titanium dioxide TiO_2 (Mahy *et al.*, 2021). The nano-sized titanium dioxide (TiO_2) was a famous photocatalyst among the metal oxides, due to its excellent efficiency, low price, physico-chemical stability, extensive disposal, safety and non-corrosive behaviour. It had three crystal forms, anatase, rutile and brookite, while the first presents the most effective photocatalytic performance (Malesic Eleftheriadou *et al.*, 2019). The main notion behind nanocomposites was to create a very broad contact between nanoscale building components and the polymer matrix (Muna *et al.*, 2021). The use of natural dye in this research was as a photosensitizer. When applied to polymers to increase optical and structural characteristics for solar cell applications, plant dye was a very safe, cost-effective, and bioactive component. Semi-conducting oxide nanostructures had a large band gap and high surface area, such as TiO_2 nanoparticles. The addition of nanoparticles to a nanocomposites matrix containing a natural dye could boost free electron scattering, resulting in the formation of a new position that limits electron mobility and enhances light absorption (Adedokun *et al.*, 2016). In this study, the optical (A, T, R, E_g) properties of the (PVA/TiO_2/dye) nanocomposite were examined and used for optical microscopy and FTIR spectroscopy.

MATERIALS AND METHODS

Titanium dioxide (TiO_2) was from Zhengzhou Dongyao Nano Materials Co. Powder Ltd, a Chinese manufacturer with nano particle sizes of 30 nm, a density of 4.23 g/cm^3, a white hue, and a high purity (99.99%). PVA was a white granular type of polyvinyl alcohol with a molecular weight of 26,300-30,000 g/mol. Shanghai Kaidu Industrial Development Co, Ltd, China was the source of polyvinyl alcohol. The active part of crocus was the stigma of the flower, which was carefully removed from the blooming flowers and dried in the shade and then over a low heat. The crocus was extracted by filtering it, then concentrated by boiling at 75°C and eliminating 20% of the water to preserve its perfume. Finally, the dehydration was completed in a dryer (oven) at 75°C for 10 h, resulting in a dry paste that was crushed to generate the dye powder. One gram of polyvinyl alcohol was dissolved completely in 20 ml of water in a glass beaker for one hour at 90°C with constant stirring. After the pure sample had been dissolved, a small amount of Titanium dioxide nanoparticles (0.30) wt. per cent was added, followed by placing the glass beaker in an ultrasonic device to disperse the Titanium dioxide and mixing with different ratios (1, 2, 3 and 4) ml of crocus dye per 20 ml (PVA-TiO_2) and forming diverse samples. Then, utilizing drops of each nanocomposites that had been created, a vacuum spin coater was used to create films with a thickness of 774±3 nm on glass substrates. The substrates were glass slides with a surface area of (2.5 × 7.5) cm^2 and a thickness of 0.1 cm.

When light fell on material, several reactions occurred as a result of the interaction of the incident rays with the material, including absorption, as part of the incident light was absorbed by the material and turned into heat, and the other part passed through the material and was called transmitted light, and the remaining part suffering a process of reflection and was called reflected light (Vu and Hoang, 2021). As long as the spectrophotometer calculated the relative value of the transmitted light, this value had a close relationship with the absorbance according to Lambert-Beer law (Alsaad *et al.*, 2022) :

$$A = \log (I_o / I_A) \quad ...(1)$$

The amount (I/I^o) was called the transmittance (T), which can be defined as the ratio between the light energy that passes from the surface to the light energy falling on the surface. The reflectivity was defined as the ratio of the reflected light energy to the incident light energy. The value of the reflectivity with respect to the perpendicular fall at the angle of incidence was given (Abel *et al.*, 2021) as :

$$R = \frac{(n - 1)^2}{(n + 1)^2} \quad ...(2)$$

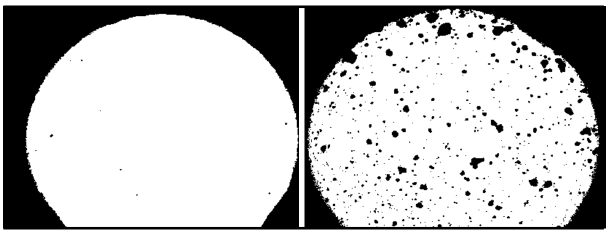
Direct electrical transitions were calculated and quantity of optical energy gap ($E_{opt.}$) was calculated using the relationship (3) :

$$A h\upsilon = \beta (h\upsilon - Eg)^r \quad ...(3)$$

If the transition occurred between states of the same wave vector, the transition was called direct transition (Mohammed *et al.*, 2021).

RESULTS AND DISCUSSION

Images of PVA and PVA/TiO2/crocus dye nanocomposites films acquired for samples at magnification power (10x) revealed a noticeable difference in the samples as shown in the photographs (Fig. 1A and B) showing polyvinyl alcohol (PVA) nanocomposites (A) and (PVA+TiO2) nanocomposites (B). Because TiO2 particles absorbed incident light, they appeared as black dots. Nanoparticles created a continuous network inside polymers. This network's routes that allowed charge carriers to move via them inside the nanocomposites. This reduced the optical energy gap (Arata *et al.*, 2018).



(A) PVA **(B) PVA/TiO_2/dye**

Fig. 1. Photomicrographs (10x) for (A) for (PVA) and (B) for (PVA/TiO_2/crocus dye) for samples magnification power (10x).

Some observable changes were observed in the spectral features of the samples in the range

500-1100/cm (fingerprint region) apart from new absorption bands and slight changes in the intensities of some absorption bands. The new bands might be correlated likewise with defects induced by the charge transfer reaction between the polymer chain and the nanomaterials and different concentration of crocus dye (Al-Abdulaal and Yahia, 2021). Infrared spectroscopy was used to confirm the presence of functional groups in a composite and not for determination of the structure of a composite (Nnorom and Onuegbu, 2019). The vibrational peaks (Fig. 2) at 3387, 3325.28, 1705.07 and 1080.14/cm were assigned to O–H stretching, C–H stretching, C–H bend of CH_2, C-O and CH rocking of PVA/TiO2/crocus dye, respectively and another vibrational peaks for concentrations of nanocomposites (Al-Abdulaal and Yahia, 2021). After increased concentration of natural crocus dye, some polymer chains were broken and other chains formed. Increase in concentration generated new bonds in this range. Decreasing the FT-IR spectrum in the range of 3387 to 3367.71/cm showed the produced polymer chains which corresponded to O–H stretching and C–H stretching bond (Fig. 3; Haji *et al.*, 2018). These results indicated a strong cross linking between the dye and the nanocomposite.

The absorption spectra of PVA/TiO_2/crocus dye nanocomposites were a function of incoming light wavelength (Fig. 4). The absorbance for all films had high values at the fundamental absorption edge (340 nm), as the appearance of a peak for all films at 440 nm, which was

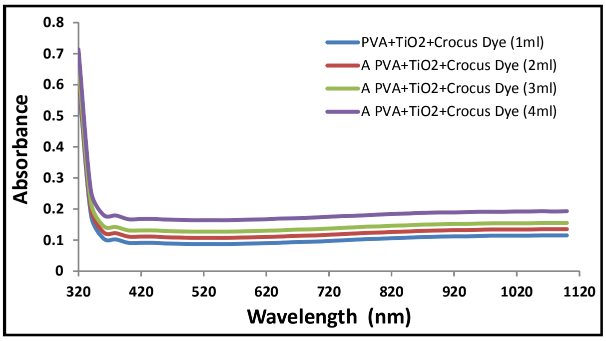


Fig. 4. The absorbance as function of wavelength for PVA/TiO_2/crocus dye nanocomposite.

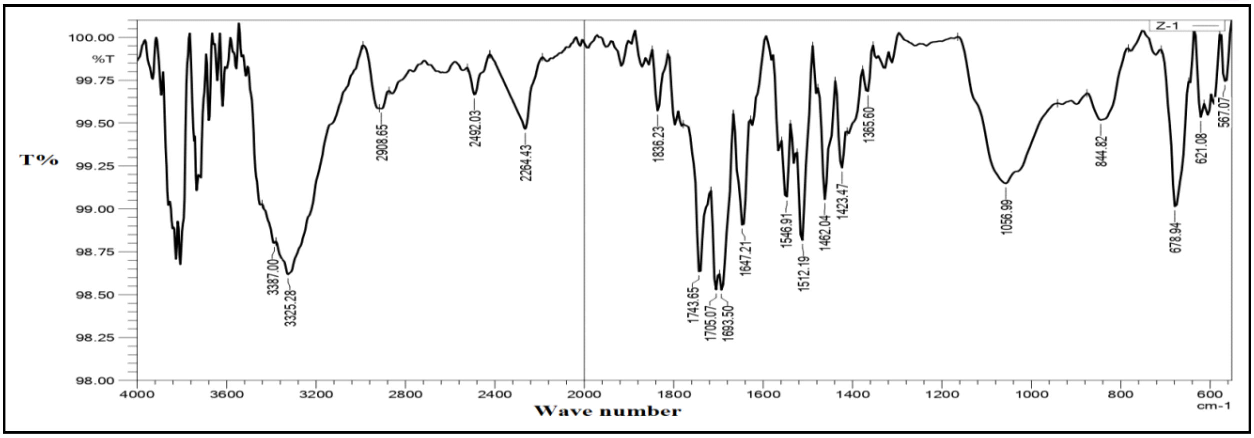


Fig. 2. FT-IR of PVA/TiO_2/1 ml crocus dye.

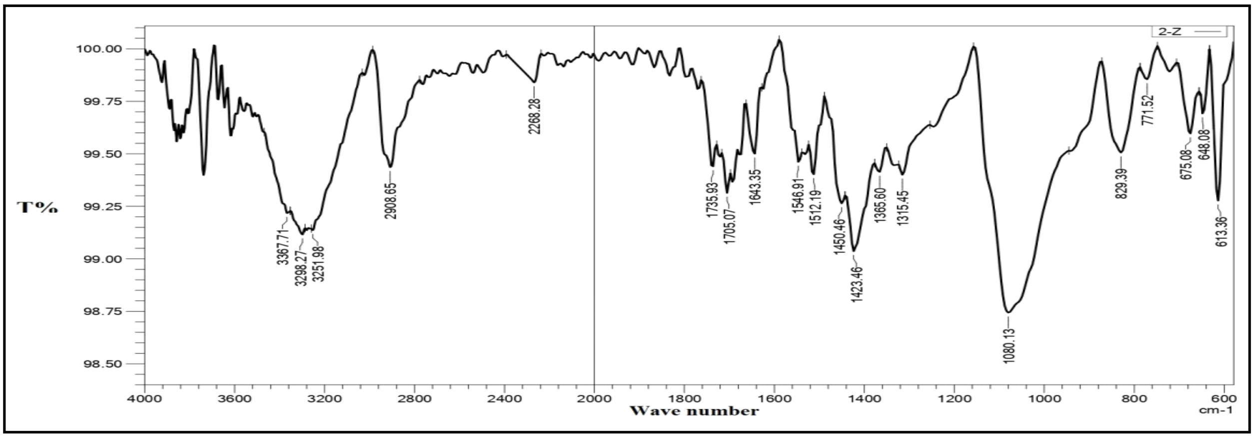


Fig. 3. FT-IR of PVA/TiO_2/4 ml crocus dye.

due to the crocus dye (Arof *et al.*, 2017). When incoming photons had insufficient energy to interact with atoms at long wavelengths, the photon will transmit. The interaction between incoming photon and substance occurred as the wavelength lowered, and the absorbance increased. In other words, as the crocus dye concentration rose, so did the absorption (Maurya *et al.*, 2018).

Fig. 5 shows that the composite had the greatest transmittance of 81.5 at a concentration of 1 ml. Then it started to decrease. Transmittance decreased when the concentration of natural crocus dye increased due to the addition of dye. It was concluded that light did not spread, implying that the thin layers were homogeneous and optically flat (Maurya *et al.*, 2018; Simion and Ioan, 2022). Further, grapheme was employed as gas sensors (Khudair and Mohaimeed, 2020).

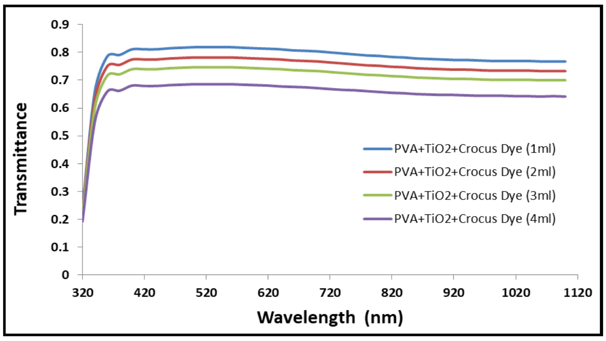


Fig. 5. The transmittance as function of wavelength for PVA/TiO$_2$/crocus dye nanocomposite.

Energy gap (3.7, 3.68, 3.62 and 3.58) eV decreased with increasing concentration of natural crocus dye (Fig. 6). This was due to the creation of localized levels, so the electron moved in two stages from the valence gap to those levels and then to the conduction band.

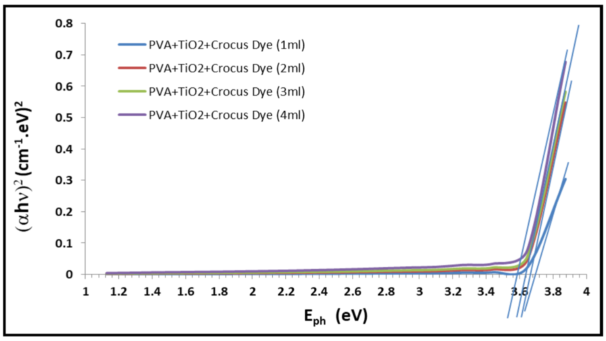


Fig. 6. Graphically relation for the allowed direct transition between $(\alpha h\upsilon)^2$ and photon energy (hv) of (PVA/TiO2) and different concentration of crocus dye.

This was showed by the optical microscope images in the formation of a network inside the polymer that allowed the passage of electrons (Simion and Ioan, 2022). Nanoparticles were one of today's and tomorrow's most essential technologies (Alsultany and Mohaimeed, 2021).

CONCLUSION

Effect of crocus plant dye on morphological properties was estimated through measurements of FT-IR. After increasing the concentration of natural crocus dye, some polymer chains had been broken and some other chains had been formed. Increase concentration generated new bonds in this range. Decreasing the FT-IR spectrum in the range of 3387 to 3367.71/cm showed that the produced polymer chains corresponded to O–H stretching and C–H stretching bond. PVA/TiO$_2$/crocus dye nanocomposites could be used as a cover of solar cell because it had transmittance over 81%, and the energy gap (E_g) decreased by increasing concentration of crocus dye (3.7-3.58) eV.

REFERENCES

Arata, Abdulameer Khalaf, Dalal, Hassan Abdulkadhimb and Maher, Hasan Rashid (2018). Study of electrical properties of poly (Vinyl alcohol)/Alumina (PVA/Al2O3) nanocomposites. *J. Univ. Babylon, Pure and Appl. Sci.* **26** : 095-100.

Abel, S., Leta Tesfaye, J., Kiran, R., Deepak, T., Usha Ruby, A., Venkatesh, S. and Krishnaraj, R. (2021). Studying the effect of metallic precursor concentration on the structural, optical and morphological properties of zinc sulfide thin films in photovoltaic cell applications. *Adv. Mater. Sci. Eng.* **2021** : 1-6.

Adedokun, O., Titilope, K. and Awodugba, A. (2016). Review on natural dye-sensitized solar cells (DSSCs). *Int. J. Eng. Tec.* **2** : 34-41.

AlAbdulaal, T. H. and Yahia, I. S. (2021). Analysis of optical linearity and non-linearity of Fe^{3+}-doped PMMA/FTO polymeric films : New trend for optoelectronic polymeric devices. *Physica B : Condensed Matter* **601.** *DOI : 10.1016/J.PHYSB.2020.412628.*

Alsaad, A. M., Ahmad, A. A., Qattan, I. A., El-Ali, A. R., Al-Fawares, S. A. and Al-Bataineh, Q. M. (2021). Synthesis of optically tunable and thermally stable PMMA-PVA/CuO NPs hybrid nanocomposite thin films. *Polymers*

(Basel) **13** : 1715: *https://doi.org/10.3390/polym13111715.*

Alsaad, A. M., Al-Dairy, A. R., Ahmad, A. A., El-Ali, A. R., Al-Fawares, S. A. and Al-Bataineh (2022). Synthesis and characterization of as-grown doped polymerized (PMMA-PVA)/ ZnONPs hybrid thin films. *Polym. Bull.* **79** : 2019-2040.

Alsultany, S. J. and Mohaimeed, A. A. (2021). Role of nanoparticles synthesized from bacteria as antimicroorganism : A review. *Iraqi J. Nanotechnology* **2** : 44-53.

Arof, A. K., Mat Nor, N. A., Ramli, N. R., Aziz, N., Noor, I. M. and Taha, R. M. (2017). Utilization of saffron (*Crocus sativus* L.) as sensitizer in dye-sensitized solar cells (DSSCs). *Opt. Quant. Electron.* **49** : 37. *https://doi.org/10.1007/s11082-016-0882-6.*

Bahaa, H. Rabee and Nasser, Jabar (2017). The optical properties of copper oxide nanoparticles with (Polyvinyl Alcohol-Polyethylene Glycol) blend. *J. Chem. Pharm. Res.* **9** : 310-314.

Haji, A., Nasiriboroumand, M. and Qavamnia, S. S. (2018). Cotton dyeing and antibacterial finishing using agricultural waste by an eco-friendly process optimized by response surface methodology. *Fibers Polym.* **19** : 2359-2364.

Mahy, J. G., Lejeune, L., Haynes, T., Lambert, S. D., Marcilli, R. H. M., Fustin, C. A. and Hermans, S. (2021). Eco-friendly colloidal aqueous sol-gel process for TiO_2 synthesis : The peptization method to obtain crystalline and photoactive materials at low temperature. *Catalysts* **11** : 768.

Malesic Eleftheriadou, N., Evgenidou, E., Kyzas, G. Z., Bikiaris, D. N. and Lambropoulou, D. A. (2019). Removal of antibiotics in aqueous media by using new synthesized bio-based poly (ethylene terephthalate)-TiO2 photocatalysts. *Chemosphere* **234** : 746-755.

Maurya, I. C., Singh, S. and Neetu (2018). Dye-sensitized solar cells employing extracts from four cassia flowers as natural sensitizers : Studies on dye ingredient effect on photovoltaic performance. *J. Electron. Mat.* **47** : 225-232.

Mohammed, M. I., Jilani, W. and Bouzidi, A. (2021). Synthesis, optical properties and impedance spectroscopy of Na_2TeO_3 doped polyvinyl alcohol as novel polymeric electrolyte films. *Opt. Quant. Electron* **53** : 280. *https://doi.org/10.1007/s11082-021-02937-5.*

Muna, A., Abu-Dalo, Saja, A., Al-Rosan and Borhan, A. Albiss (2021). Photocatalytic degradation of methylene blue using polymeric membranes based on cellulose acetate impregnated with Zno nanostructures. *Polymers (Basel)* **13** : 3451.

Nnorom, Onyekachi Onyinyechi and Onuegbu, Genevive Chinyere (2019). Authentication of rothmanniawhitfieldii dye extract with FTIR spectroscopy. *J. Textile Sci. Tech.* **5** : 38-47.

Khudair, Salah Abdul Mahdi and Mohaimeed, Ameen Alwan (2020). Gas sensor investigations through adsorption of toxic gas molecules on single and double vacancy graphene. *Neuro. Quantology* **18** : 87-95.

Simion, Jitian and Ioan, Bratu (2022). Changing the optical properties of poly (methyl methacrylate) superficial films during UV irradiation. *Int. J. Rapid Comm.* **55.** *https://doi.org/10.1080/00387010.2022.2046105.*

Vu, T. T. and Hoang, H. H. (2021). Investigating the effect of pulsed fiber laser parameters on the roughness of aluminium alloy and steel surfaces in cleaning processes. *Lasers Manuf. Mater Process* **8** : 113-124.