Наносистеми, наноматеріали, нанотехнології
Nanosistemi, Nanomateriali, Nanotehnologii
2024, т. 22, № 3, сс. 727–738
https://doi.org/10.15407/nnn.22.03.727

PACS numbers: 78.20.Ci, 78.66.Sq, 78.67.Sc, 81.07.Pr, 81.40.Tv, 82.35.Np, 85.60.-q

Effect of ZrO_2–CuO Nanofiller on the Optical Constants and Optical Conductivity of Biopolymer

Majeed Ali Habeeb[1], Idrees Oreibi[2], and Rehab Shather Abdul Hamza[1]

[1]*College of Education for Pure Sciences,*
Department of Physics,
University of Babylon,
Hillah, Iraq
[2]*Directorate of Education Babylon,*
Ministry of Education,
Babylon, Iraq

Creating polymer nanocomposite specimens is carried out using the solution-casting technique. The specimens are comprised of a host matrix of polyvinyl alcohol (PVA), in which varying concentrations of zirconium oxide (ZrO_2) and copper oxide (CuO) nanoparticles are incorporated, spanning a range from 0 to 6 wt.%. The nanostructures composed of PVA–ZrO_2–CuO exhibit notable attributes, such as low expenses, enhanced resistance to corrosion, favourable optical properties, and a relatively lightweight nature compared to alternative nanosystems. The optical properties are measured within the wavelength range (λ) from 200 nm to 840 nm. Optical properties show that the absorption coefficient, refractive index, and dielectric-constant real and imaginary parts for PVA–ZrO_2–CuO nanocomposite increase with increasing concentrations of the ZrO_2–CuO nanoparticles; so, the optical parameters at wavelength $\lambda = 400$ nm: absorption coefficient (α), refractive index (n), extinction coefficient (k), real (ε_1) and imaginary (ε_2) parts of dielectric constants, and optical conductivity (σ_{op}) for PVA are enhanced by about 1540%, 100%, 2216%, 302%, 1116%, and 3025%, respectively, with adding of 6 wt.% ZrO_2–CuO nanoparticles. The performance of the PVA–ZrO_2–CuO nanocomposites suggests that they possess favourable characteristics as optical nanomaterials in the domains of electronics and optics.

Створення зразків полімерних нанокомпозитів проводили методом лиття з розчину. Зразки включали головну матрицю з полівінілового спирту (ПВС), в яку було втілено різні концентрації наночастинки оксиду Цирконію (ZrO_2) й оксиду Купруму (CuO), що охоплювали діяпазон від 0 до 6 масових відсотків. Наноструктури, що складаються з ПВС–ZrO_2–CuO, демонструють помітні характеристики, такі як низьку вартість, підвищену стійкість до корозії, сприятливі оптичні властивості та відносно легку природу порівняно з альтернативними наносистемами. Оптичні властивості міряли в діяпазоні довжин хвиль λ від 200 нм до 840 нм. Оптичні властивості показали, що коефіцієнт поглинання, показник заломлення та дійсна й уявна частини діелектричної проникности для нанокомпозиту ПВС–ZrO_2–CuO зростають зі збільшенням концентрації наночастинок ZrO_2–CuO; так, оптичні параметри на довжині хвилі $\lambda = 400$ нм: коефіцієнт поглинання (α), показник заломлення (n), коефіцієнт екстинкції (k), дійсна (ε_1) й уявна (ε_2) частини діелектричної проникности та оптична провідність (σ_{op}) для ПВС збільшуються приблизно на 1540%, 100%, 2216%, 302%, 1116% і 3025% відповідно з додаванням наночастинок ZrO_2–CuO (6 мас.%). Експлуатаційні показники нанокомпозитів ПВС–ZrO_2–CuO наводять на думку, що вони мають сприятливі характеристики як оптичні наноматеріяли в областях електроніки й оптики.

Key words: PVA, ZrO_2, CuO, nanocomposites, optical properties.

Ключові слова: полівініловий спирт, ZrO_2, CuO, нанокомпозити, оптичні властивості.

(Received 21 August, 2023)

1. INTRODUCTION

Since immemorial, polymers have been integral to the fabric of existence, constituting all life forms' fundamental constituents. Before the mid-twentieth century, humans had an incomplete understanding regarding polymers' fundamental characteristics and properties. Polymers have permeated various facets of human existence. Contemplating contemporary society devoid of synthetic polymeric materials and their myriad opulent and convenient attributes proves challenging. In recent years, realizing a fully customized polymer has been made possible due to advancements in comprehending the interrelationships between polymer structure and properties, emerging ground-breaking polymerization techniques, and the accessibility of innovative and cost-effective monomers [1, 2]. Polymers with corrosion resistance, low weight, and strong hardness make various products, including homemade plastics, automobile internal and external components, biomedical equipment, and satellite applications [3, 4].

A polymer blend refers to the amalgamation of two or more polymers, forming a novel material exhibiting distinct physical characteristics. Polymer mixtures, known as heat mixes, are a specific category within the broader classification of polymer mixtures. The phenomenon of heat mixing and the characteristics of thermoplastic heat mixtures have been extensively investigated in previous research [5, 6]. In contemporary times, polymers are commonly employed in electrical and electronic applications. The utilization of polymers as insulators has been attributed to their remarkable resistivity and dielectric properties. Electrical equipment utilizes polymer-based insulators to isolate electrical conductors, thereby inhibiting electric current flow efficiently. Polymer insulators are utilized in diverse fields, encompassing the manufacturing of printed circuit boards, cable sheathing materials, corrosion-resistant electronics, and wire encapsulation. Polymers offer many advantages, such as their inherent processability, exceptional flexibility, notable strength and mechanical properties, and cost-effectiveness [7, 8].

Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer. The substance exhibits a notable lack of toxicity and possesses notable attributes in terms of its application as a wound dressing and as a material for bioreactors. The semi-crystalline nature of polyvinyl alcohol is a notable attribute, as the presence of both amorphous and crystalline regions characterizes it. This structural arrangement gives rise to interfacial effects that enhance the physical properties of the material [9, 10]. Polyvinyl alcohol exhibits distinct characteristics, including biodegradability, favourable chemical stability, environmental friendliness, notable charge storage capacity, high resistance to abrasion, thermal stability, tensile strength, flexibility, elongation, ease of film processing, and cost-effectiveness in manufacturing [11, 12]. The rapid decomposition of the substance occurs at elevated temperatures. Various additives, including polymers, salts, nanocomposites, and ions, are commonly incorporated into polyvinyl alcohol (PVA) to enhance and alter its properties [13, 14]. PVA exhibits sub-optimal electrical insulation properties, yet it transforms conductivity, when doped with specific inorganic fillers [15].

Zirconium oxide (ZrO_2), commonly called zirconia, is widely recognized for its exceptional chemical and physical characteristics. Consequently, it finds extensive utility in various fields, including fuel cells, gas sensors, optoelectronics, catalysts, and corrosion-resistant materials. Zirconium dioxide (ZrO_2) has a band gap exceeding 5 eV, making it a significant luminescent material characterized by favourable optical transparency. Moreover, its considerable surface area and abundance of oxygen vacancies establish it as a promising contender for applications in photocatalysis [16, 17]. Zirconium dioxide (ZrO_2) nanoparticles exhibit notably low thermal conductivity and a high thermal expansion coefficient. Additionally, the materials above possess numerous engineering applications due to their exceptional strength, durability, thermal shock resistance, rigidity, and enhanced wear resistance [18, 19].

Copper oxide is a type of material that exhibits semiconductor behaviour and possesses distinctive optical, electrical, and magnetic characteristics. It has found diverse applications in supercapacitor development, near-infrared filtering, magnetic storage media, sensor technology, catalysis, and semiconductor devices [20, 21]. Copper oxide nanoparticles (CuO NPs) have been employed to enhance polymer films derived from petrochemical-based or bio-based polymers. The characteristics mentioned above are attributable to the remarkable surface-to-volume ratio, thermal stability, comparatively diminished toxicity, and capacity to enhance the mechanical properties of polymers [22].

This work used ZrO_2–CuO nanoparticles to improve the nanocomposite's optical properties PVA–ZrO_2–CuO. The results of this study showed a significant improvement in these characteristics.

2. MATERIALS AND METHODS

Nanocomposite films were fabricated using the casting technique, incorporating polyvinyl alcohol (PVA), zirconium oxide (ZrO_2), and copper oxide (CuO) nanoparticles. The experimental procedure involved dissolving pure polyvinyl alcohol (PVA) in 35 ml of distilled water for 35 minutes. The solution was stirred using a magnetic stirrer at a temperature of 50°C to attain a higher level of homogeneity. The polymer underwent the introduction of zirconium oxide (ZrO_2) and copper oxide (CuO) nanoparticles at different weight percentages 0%, 2%, 4%, and 6%. Following three days of air-drying the solution at room temperature, the observed outcome entailed the development of polymer nanocomposites. The nanocomposites consisting of PVA–ZrO_2–CuO were retrieved from the Petri dish and employed for measurement purposes. The optical properties of nanocomposites comprising PVA, ZrO_2, and CuO were examined using a Shimadzu U.V./1800 spectrophotometer over a wavelength range of 200–800 nm.

The evaluation of the absorption coefficient (α) of the current materials is heavily reliant on the optical transmission, reflection, and thickness of the film, as determined by the following equation [23]: $\alpha = 2.303A/d$, where d is the sample thickness, and A is the absorption of the material.

The extinction coefficient (k) was calculated using the following equation [24, 25]:

$$k = \frac{\alpha\lambda}{4\pi},$$

where λ is the wavelength. The refractive index (n) is calculated by [26] from equation:

$$n = \sqrt{4R - \frac{k^2}{(R-1)^2}} - \frac{(R+1)}{(R-1)},$$

where R is the reflectance. The dielectric constant real and imaginary parts are calculated by [27, 28] as follow: $\varepsilon_1 = n^2 - k^2$, $\varepsilon_2 = 2nk$. The optical conductivity (σ_{op}) is obtained by using the relation [29]: $\sigma_{op} = \alpha nc/4\pi$, where c is the velocity of light.

3. RESULTS AND DISCUSSION

3.1. The Optical Properties of PVA–ZrO_2–CuO Nanocomposites

Figure 1 illustrates the correlation between the absorption coefficient of nanocomposites composed of polyvinyl alcohol (PVA), zirconium dioxide (ZrO_2), and copper oxide (CuO) and the varying proportions of ZrO_2–CuO nanoparticles (NPs). The absorption coefficient increases as the ratios of ZrO_2–CuO NPs increase. This phenomenon can be attributed to the augmentation of charge carriers within the nanocomposite films. The absorption coefficient (α) for all the prepared nanocomposites exhibited the lowest values at lower energies, which can be attributed to the limited likelihood of electron transitions.

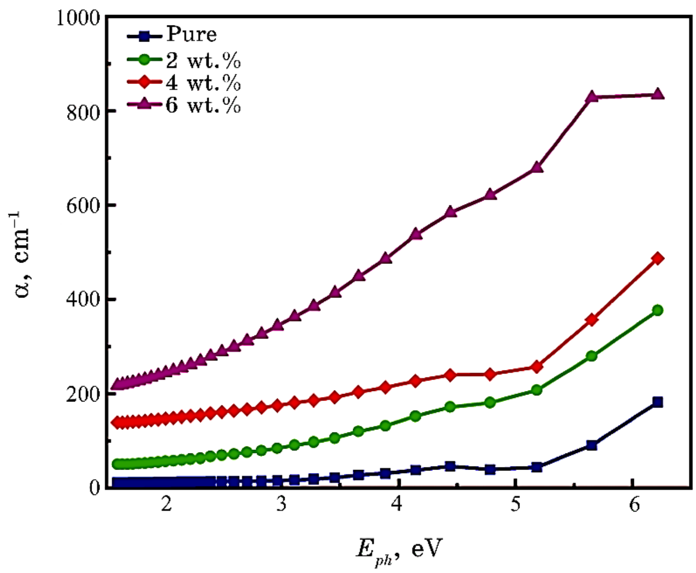

Fig. 1. Absorption coefficient for PVA–ZrO_2–CuO nanocomposites as a function of photon energy.

The probability of electron transition is high, when the energy of the incident photon increases, indicating that the energy of the photon is adequate for atom interaction. Based on the observed α

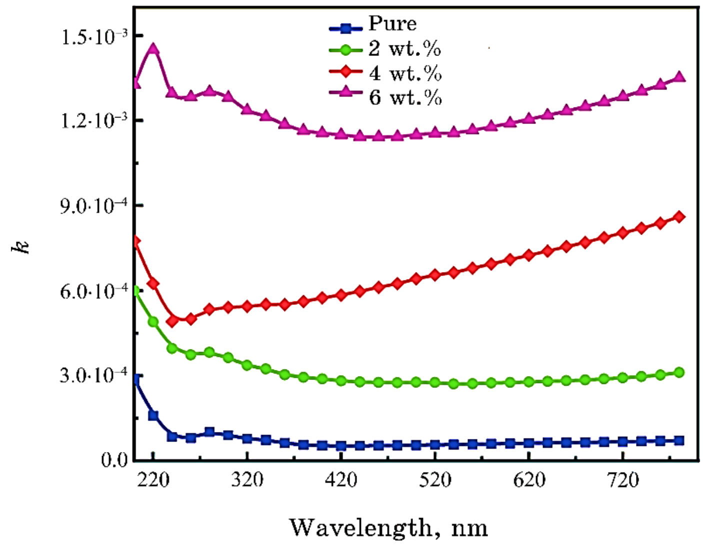

Fig. 2. Difference of extinction coefficient for PVA–ZrO_2–CuO nanocomposites with wavelength.

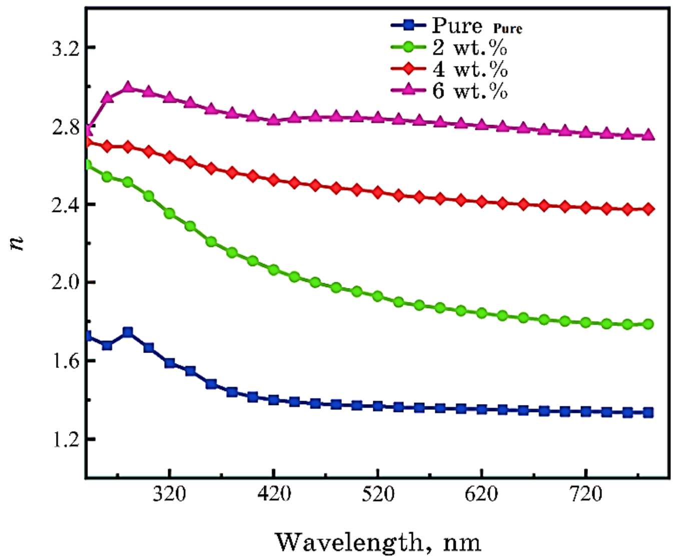

Fig. 3. The refractive index for PVA–ZrO_2–CuO nanocomposites as a function of wavelength.

values for the prepared films, which are less than 104 cm^{-1}, it can be inferred that indirect electron transitions are highly probable [30, 31].

Figure 2 illustrates the variation in the extinction coefficient concerning the wavelength. The figure observations suggest a positive correlation between the concentration of ZrO_2–CuO nanoparticles and the extinction coefficient. This relationship can be attributed to the amplified optical absorption and enhanced dispersion of photons within the polymer matrix. The extinction coefficient is contingent upon the absorption coefficient, with the former exhibiting elevated values within the UV region. Moreover, the extinction coefficient demonstrates an upward trend as the wavelength increases within the visible spectrum, extending into the near-infrared spectrum [32, 33].

The refractive index for nanocomposites consisting of PVA–ZrO_2–CuO is depicted in Fig. 3, illustrating its variation for wavelength. The figure demonstrates a positive correlation between the weight percentages of ZrO_2–CuO nanoparticles in the PVA and the corresponding refractive index; this can be attributed to the increased density of the nanocomposites. High refractive index values are observed in the ultraviolet region due to the restricted transmittance within this specific spectral range. On the other hand, the visible region exhibits low refractive index values due to increased transmittance within this specific range of wavelengths. The findings obtained by the researcher align with these results [34, 35].

The real dielectric constant (ε_1) indicates the extent to which the speed of light is reduced within a material, indicating the material's polarity. On the other hand, the imaginary dielectric constant (ε_2) signifies the ability of the dielectric to absorb energy from the electric field through dipole motion. Figures 4 and 5 depict the fluctuations in the real component (ε_1) and the imaginary component (ε_2) of the dielectric constant for both pure polymer films and nanocomposite films, as influenced by varying ratios of ZrO_2–CuO nanoparticles. These variations are observed across different photon energy levels. There is a rise in the values of ε_1 at lower photonic energies, which is subsequently followed by a distinct decline at higher energies across all nanocomposite films [36]. The dielectric constant of polymers demonstrates an increase corresponding to a fractional amplification of charges within the polymer materials.

The relationship between the real component of the dielectric constant and the refractive index can be attributed to the minimal value of the extinction coefficient. The empirical evidence indicates a positive correlation between the concentrations of ZrO_2–CuO nanoparticles and the observed increase in the real dielectric constant. The behaviour of the hypothetical dielectric constant before and af-

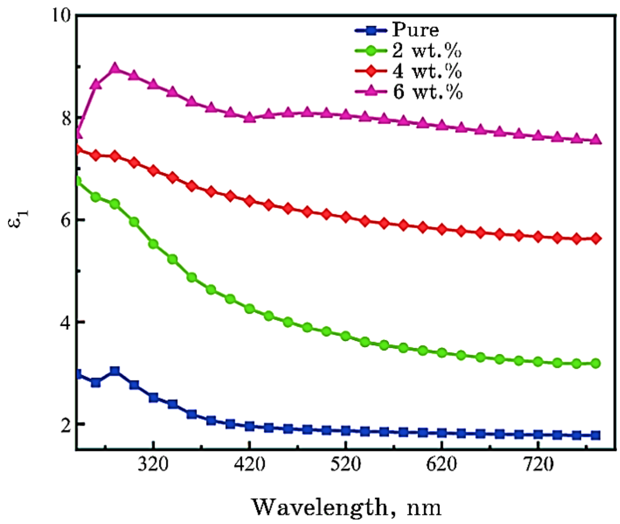

Fig. 4. The real dielectric constant (ε_1) as a function of incident wavelength for PVA–ZrO_2–CuO nanocomposites.

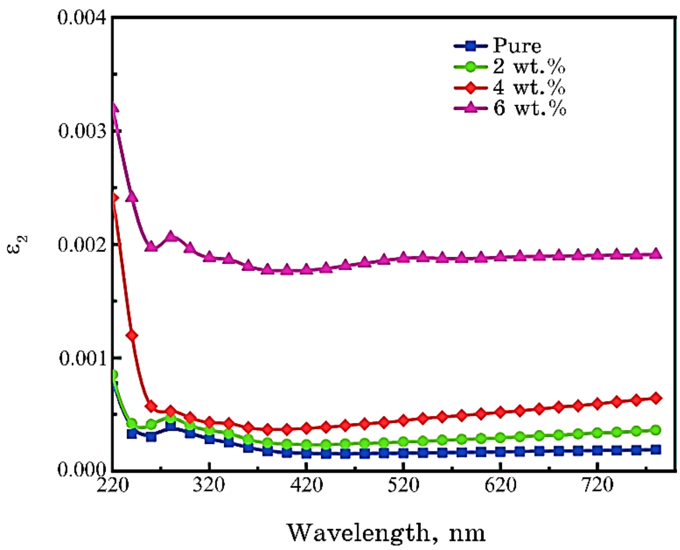

Fig. 5. The imaginary dielectric constant (ε_2) as a function of wavelength for PVA–ZrO_2–CuO nanocomposites.

ter inclusion of nanoparticles demonstrates resemblances to that of the actual dielectric constant [37, 38].

However, it is important to note that the value of the imaginary dielectric constant is lower, as depicted in Fig. 5. The correlation between the imaginary component of the dielectric constant and the extinction coefficient is of significant significance, particularly within the visible and near-infrared spectra. In the context of this specific regime, it is evident that the refractive index exhibits a consistent and unchanging value. On the contrary, the extinction coefficient exhibits an increasing trend with the rise in wavelength [39, 40].

Figure 6 demonstrates a decrease in the optical conductivity of the composite samples as the wavelength increases. The observed phenomenon exhibits a significant reliance on the wavelength of the incoming radiation on the composite samples and can be clarified by considering the concept of optical conductivity. The observed rise in optical conductivity at shorter photon wavelengths can be ascribed to the heightened absorbance exhibited by all composite samples within this particular range of the electromagnetic spectrum. Consequently, this phenomenon leads to an augmentation in charge transfer excitations [41, 42]. The optical conductivity spectra indicate that the examined samples possess the ability to propagate light within the visible and near-infrared regions.

Furthermore, incorporating ZrO_2–CuO nanoparticles leads to an observed enhancement in the optical conductivity of composites. The observed phenomenon can be ascribed to the formation of localized states within the energy gap. More precisely, an increased concentration of ZrO_2–CuO nanoparticles results in a higher density of these localized states within the band structure. Consequently, the

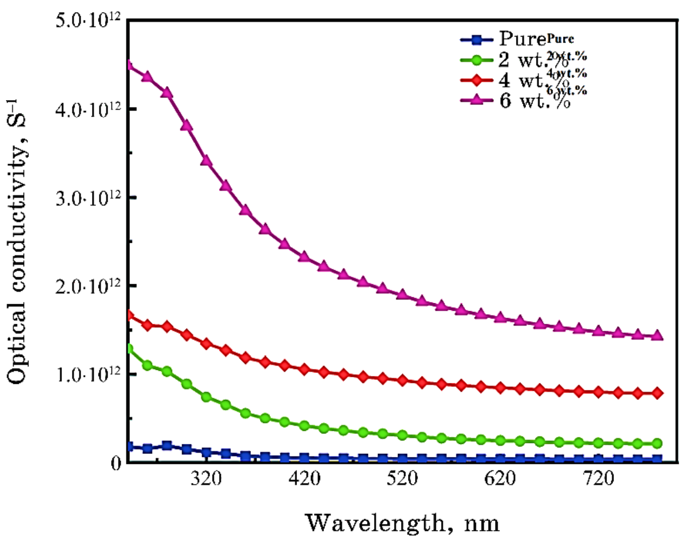

Fig. 6. Difference of optical conductivity of PVA–ZrO_2–CuO nanocomposites with wavelength.

augmentation of the absorption coefficient results in a subsequent elevation in the optical conductivity of nanocomposites comprising polyvinyl alcohol–zirconium oxide–copper oxide (PVA–ZrO_2–CuO) [43].

4. CONCLUSION

The current study involves the production of nanostructured films composed of a combination of polyvinyl alcohol (PVA), zirconium dioxide (ZrO_2), and copper oxide (CuO) through the solution casting method. A comprehensive investigation has been conducted on the optical characteristics of nanostructures composed of polyvinyl alcohol (PVA), zirconium dioxide (ZrO_2), and copper oxide (CuO). The analysis of optical properties revealed that the absorption coefficient, refractive index, and dielectric constant (both real and imaginary components) of the PVA–ZrO_2–CuO nanocomposite exhibit a positive correlation with the concentrations of ZrO_2–CuO nanoparticles. These findings indicate significant improvements in the optical properties of the nanocomposite. The extinction coefficient exhibits elevated values within the UV-range, demonstrating a positive correlation with increasing wavelength within the visible spectrum, extending into the near-infrared spectrum. Moreover, composites' optical conductivity increases, when ZrO_2–CuO nanoparticles are incorporated. The findings of this study indicate that the material exhibits potential suitability for various optoelectronic applications.

REFERENCES

1. D. R. Paul and L. M. Robeson, *Polymer*, **49**, No. 15: 3187 (2008); https://doi.org/10.1016/j.polymer.2008.04.017
2. A. H. Hadi and M. A. Habeeb, *Journal of Mechanical Engineering Research and Developments*, **44**, No. 3: 265 (2021); https://jmerd.net/03-2021-265-274/
3. N. Othman, N. A. Azahari, and H. Ismail, *Malaysian Polymer Journal*, **6**, No. 6: 147 (2011).
4. M. A. Habeeb and Z. S. Jaber, *East European Journal of Physics*, **4**: 176 (2022); doi:10.26565/2312-4334-2022-4-18
5. M. A. Habeeb, *European Journal of Scientific Research*, **57**, No. 3: 478 (2011).
6. Q. M. Jebur, A. Hashim, and M. A. Habeeb, *Egyptian Journal of Chemistry*, **63**: 719 (2020); https://dx.doi.org/10.21608/ejchem.2019.14847.1900
7. S. Muntaz Begum, M. Rao, and R. Ravikumar, *Journal of Inorganic and Organometallic Polymers and Materials*, **23**: 350 (2013); https://doi.org/10.1007/s10904-012-9783-8
8. S. M. Mahdi and M. A. Habeeb, *Optical and Quantum Electronics*, **54**, Iss. 12: 854 (2022); https://doi.org/10.1007/s11082-022-04267-6

9. N. Hayder, M. A. Habeeb, and A. Hashim, *Egyptian Journal of Chemistry*, **63**: 577 (2020); doi:10.21608/ejchem.2019.14646.1887
10. N. Kumar, V. Crasta, and B. Praveen, *Physics Research International*, **2014**: Article ID 742378-1 (2014); https://doi.org/10.1155/2014/742378
11. M. A. Habeeb, A. Hashim, and N. Hayder, *Egyptian Journal of Chemistry*, **63**: 709 (2020); https://dx.doi.org/10.21608/ejchem.2019.13333.1832
12. A. Hashim, M. A. Habeeb, and Q. M. Jebur, *Egyptian Journal of Chemistry*, **63**: 735 (2020); https://dx.doi.org/10.21608/ejchem.2019.14849.1901
13. S. M. Mahdi and M. A. Habeeb, *Physics and Chemistry of Solid State*, **23**, No. 4: 785 (2022); doi:10.15330/pcss.23.4.785-792
14. C. V. Reddy, B. Babu, I. N. Reddy, and J. Shim, *Ceramics International*, **44**, No. 6: 6940 (2018); https://doi.org/10.1016/j.ceramint.2018.01.123
15. M. A. Habeeb and W. S. Mahdi, *International Journal of Emerging Trends in Engineering Research*, **7**, No. 9: 247 (2019); doi:10.30534/ijeter/2019/06792019
16. M. A. Habeeb and R. S. Abdul Hamza, *Journal of Bionanoscience*, **12**, No. 3: 328 (2018); https://doi.org/10.1166/jbns.2018.1535
17. Q. Zhang, K. Zhang, D. Xu, G. Yang, H. Huang, F. Nie, C. Liu, and S. Yang, *Progress in Materials Science*, **60**: 208 (2014); https://doi.org/10.1016/j.pmatsci.2013.09.003
18. M. A. Habeeb, A. Hashim, and N. Hayder, *Egyptian Journal of Chemistry*, **63**: 697 (2020); https://dx.doi.org/10.21608/ejchem.2019.12439.1774
19. M. A. Habeeb and W. K. Kadhim, *Journal of Engineering and Applied Sciences*, **9**, No. 4: 109 (2014); doi:10.36478/jeasci.2014.109.113
20. M. Hdidar, S. Chouikhi, A. Fattoum, M. Arous, and A. Kallel, *Journal of Alloys and Compounds*, **750**: 375 (2018); https://doi.org/10.1016/j.jallcom.2018.03.272
21. M. A. Habeeb, *Journal of Engineering and Applied Sciences*, **9**, No. 4: 102 (2014); doi:10.36478/jeasci.2014.102.108
22. H. J. Park, A. Badakhsh, I. T. Im, M.-S. Kim, and C. W. Park, *Applied Thermal Engineering*, **107**: 907 (2016); https://doi.org/10.1016/j.applthermaleng.2016.07.053
23. S. M. Mahdi and M. A. Habeeb, *Digest Journal of Nanomaterials and Biostructures*, **17**, No. 3: 941 (2022); https://doi.org/10.15251/DJNB.2022.173.941
24. G. A. Eid, A. Kany, M. El-Toony, I. Bashter, and F. Gaber, *Arab. J. Nucl. Sci. Appl*, **46**, No. 2: 226 (2013).
25. A. H. Hadi and M. A. Habeeb, *Journal of Physics: Conference Series*, **1973**, No. 1: 012063 (2021); doi:10.1088/1742-6596/1973/1/012063
26. Q. M. Jebur, A. Hashim, and M. A. Habeeb, *Egyptian Journal of Chemistry*, **63**, No. 2: 611 (2020); https://dx.doi.org/10.21608/ejchem.2019.10197.1669
27. G. Aras, E. L. Orhan, I. F. Selçuk, S. B. Ocak and M. Ertuğrul, *Procedia–Social and Behavioral Sciences*, **95**: 1740 (2015); https://doi.org/10.1016/j.sbspro.2015.06.295
28. M. A. Habeeb and A. H. Mohammed, *Optical and Quantum Electronics*, **55**, Iss. 9: 791 (2023); https://doi.org/10.1007/s11082-023-05061-8
29. M. H. Dwech, M. A. Habeeb, and A. H. Mohammed, *Ukr. J. Phys.*, **67**, No. 10: 757 (2022); https://doi.org/10.15407/ujpe67.10.757

30. M. Martin, N. Prasad, M. M. Siva lingam, D. Sastikumar, and B. Karthikeyan, *Journal of Material Science: Material in Electronics*, **29**: 365 (2018); https://doi.org/10.1007/s10854-017-7925-z
31. M. A. Habeeb and W. H. Rahdi, *Optical and Quantum Electronics*, **55**, Iss. 4: 334 (2023); https://doi.org/10.1007/s11082-023-04639-6
32. R. Dalven and R. Gill, *J. Appl. Phys.*, **38**, No. 2: 753 (1967); doi:10.1063/1.1709406
33. R. N. Bhagat and V. S. Sangawar, *Int. J. Sci. Res. (IJSR)*, **6**: 361 (2017).
34. R. S. Abdul Hamza and M. A. Habeeb, *Optical and Quantum Electronics*, **55**, Iss. 8: 705 (2023); https://doi.org/10.1007/s11082-023-04995-3
35. A. Goswami, A. K. Bajpai, and B. K. Sinha, *Polym. Bull.*, **75**, No. 2: 781 (2018); https://doi.org/10.1007/s00289-017-2067-2
36. S. M. Mahdi and M. A. Habeeb, *AIMS Materials Science*, **10**, No. 2: 288 (2023); doi:10.3934/matersci.2023015
37. I. Oreibi and J. M. Al-issawe, *Turkish Computational and Theoretical Chemistry*, **7**, No. 2: 12 (2023); https://doi.org/10.33435/tcandtc.1161253
38. M. A. Habeeb and R. S. A. Hamza, *Indonesian Journal of Electrical Engineering and Informatics*, **6**, No. 4: 428 (2018); doi:10.11591/ijeei.v6i1.511
39. N. K. Al-Sharifi and M. A. Habeeb, *East European Journal of Physics*, **2**: 341 (2023); doi:10.26565/2312-4334-2023-2-40
40. V. Suryawanshi, A. S. Varpe, and M. D. Deshpande, *Thin Solid Films*, **645**: 87 (2018); https://doi.org/10.1016/j.tsf.2017.10.016
41. Z. S. Jaber, M. A. Habeeb, and W. H. Radi, *East European Journal of Physics*, **2**: 228 (2023); doi:10.26565/2312-4334-2023-2-25
42. A. A. Mohammed and M. A. Habeeb, *East European Journal of Physics*, **2**: 157 (2023); doi:10.26565/2312-4334-2023-2-15
43. M. I. Baker, S. P. Walsh, Z. Schwartz, and B. D. Boyan, *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, **100**, No. 5: 1451 (2012); https://doi.org/10.1002/jbm.b.32694