Synthesis of PVA-Fe_2O_3-TiO_2 hybrid structure for biomedical application

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This work investigates the structure, morphology, and optical properties of TiO2 nanoparticles embedded in a Fe2O3–PVA composite matrix. The samples were examined using a variety of techniques, including field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), absorption and transmission spectra, and Fourier transformation infrared (FTIR). Crystallography information revealed the presence of TiO2 doesn't effect in the crystal structure of PVA-Fe2O3. The manufactured composites demonstration strong absorption in the range of 440–570 nm. It is important that the highest absorption of these composites gradually shifted to the shorter wavelength region with presence of TiO2. PVA-Fe2O3 is highly transparent with transmittance of around 85 % in range 600-800 nm. After addition of 2.5 % by weight of TiO2 nanoparticles, the transmittance of nanocomposite drops to 75% in the same range of wavelength . Further addition of nanoparticles reduced the percentage transmittance to 68%. The results specify that as the TiO2 ratio increases, the band gap be wider.

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1. Introduction

Magnetic nanoparticles (MNPs) are a type of nanoparticle that can be manipulated by applying a magnetic field to them. MNPs are often made up of magnetic elements including iron, nickel, and cobalt, as well as their oxides. Magnetic resonance imaging (MRI), targeted medication and gene delivery, tissue engineering, cell tracking, and bioseparation have all benefited from MNPs' unique capacity to be steered by an external magnetic field [1]. Thus, magnetic Nanoparticles has several remarkable magnetic properties, including being superparamagnetic and having a high coercivity and poor Curie temperature and high magnetic susceptibility, etc. A wide range of areas, such as magnetic fluids, data storage, catalysis, and biotechnology are all demonstrating an increased interest in magnetic nanoparticles [2-6].

Polymer based composite nanomaterials are of tremendous scientific and technological interest because of their unique optical, electrical, and mechanical capabilities. A wide variety of uses exist for these materials, including optoelectronic components and magneto-optic data storages [7-9]. Many efforts have been made to enhance the optical properties of polymer nanobased composites by reinforcing polymers with metal, semiconductor, carbon nanotubes, and magnetic nanoparticles [10-16].

The non-toxic role of Fe2O3 nanoparticles in biological systems makes them appealing in biomedical applications. Fe2O3 nanoparticles are magnetic and semiconductor, allowing for multiple biological uses [17]. Fe2O3 nanoparticle has a band gap equal 2.1–2.2 ev [18]. The effect of eco-friendly iron oxide nanoparticles on biological systems can be studied. Many researchers have attempted various biological uses. [19].

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Because of its exceptional features, such as super paramagnetism and size, iron oxide nanoparticles (IONPs) have greatly benefited from their use in medical and biotechnological advancements, such as magnetic resonance imaging, cell separation and detection and tissue restoration. In-progress studies aim to decrease drug concentrations, toxicity, and side effects while boosting the efficacy of treatments based on IONPs [20].

PVA-Fe2O3 and PVA-Fe2O3-TiO2 nanocomposites were synthesized using chemical technique in this study. Each of the nanocomposites was studied in terms of morphological structure, particle size distribution and band gap energies

2. Experimental part

2.1. Chemicals

Polyvinyl alcohol ((C2H4O)x), Iron(III) chloride (FeCl3), Sodium hydroxide (NaOH) and Titanium dioxide (TiO2).

2.2. Preparation of PVA-Fe_2O_3 Nanocomposite

The preparation of Fe2O3 capped with PVA has been carried out according our work in ref [10].

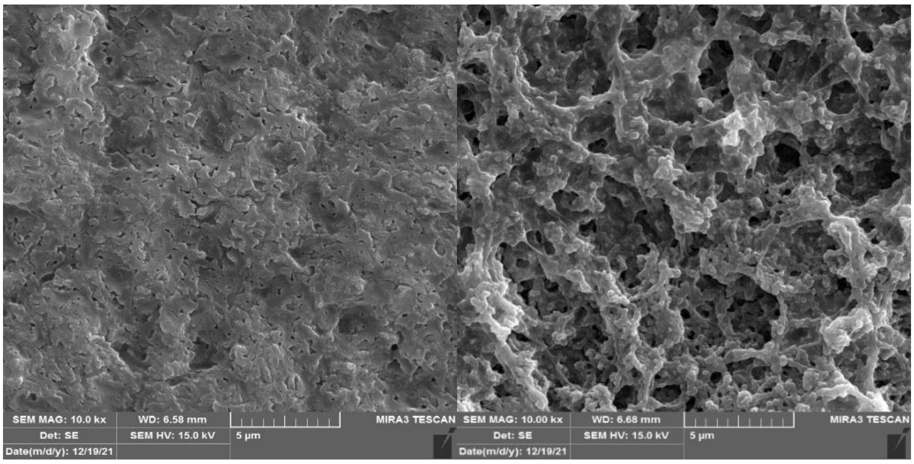
2.3. Preparation of PVA-Fe_2O_3-TiO2 Nanocomposite

Nanocomposite materials made by using blending two mass ratio of TiO2 with PVA-Fe2O3

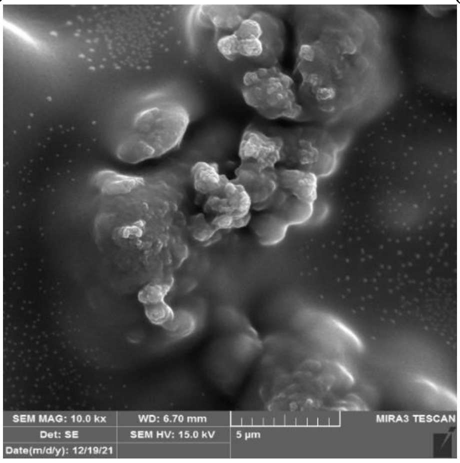
F pure is the PVA-Fe2O3, F1 is PVA-Fe2O3 with 2.5% TiO2 NPs and F2 is PVA-Fe2O3 with 5% TiO2 NPs.

3. Results and discussions

The surface morphologies of the prepared samples were studied using Scanning Electron Microscope All the nanoparticles are spherical in shape. According to Fig. 1(a–c), which shows FESEM images of produced composites, the sample has porous and aggregated morphology, which is thought to improve the sample's properties. The photos also revealed particles of about identical size in both large and tiny sizes. When the ratio of TiO2 increase in the hybrid matrix noticeable agglomeration appeared and that shown in figure 1c which represent the PVA-Fe2O3 with 5% TiO2 NPs. which is possess a compact morphology of cauliflower type similar to what get in ref. [21].



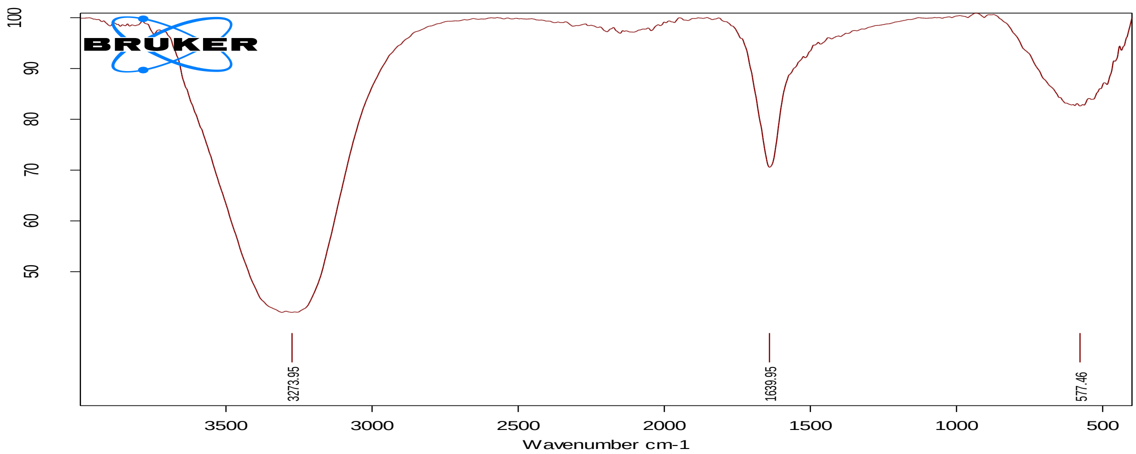
(a) *(b)*



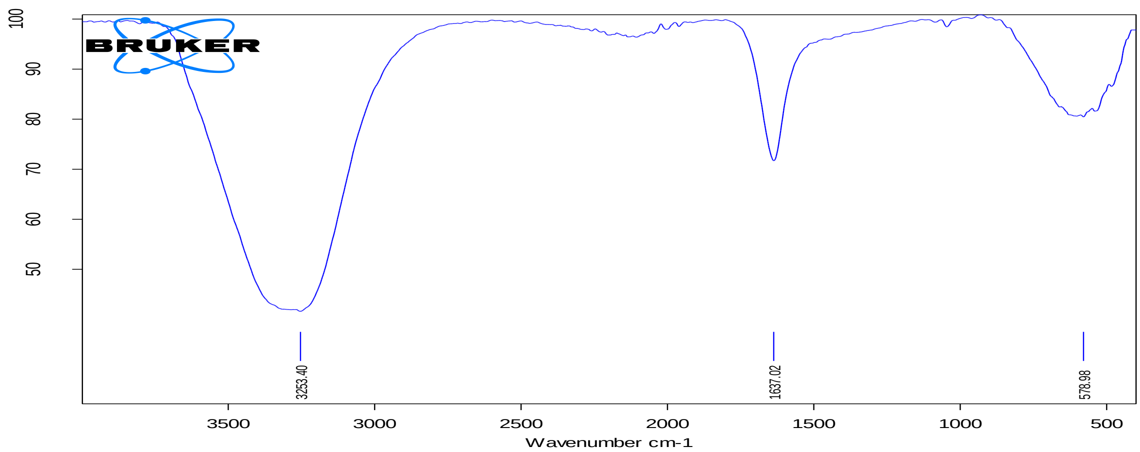
(c)

Fig. 1. FESEM images of (a) PVA-Fe2O3 (b) PVA-Fe2O3 with 2.5% TiO2 (c) PVA-Fe2O3 with 5 % TiO2.

The formation of nanoparticles was further confirmed by FT-IR spectroscopy. (Fig. 2a) shows FT-IR spectra of PVA-Fe2O3. the strong absorption peaks at 577 cm-1 can be attributed to the Fe–O band vibrations [22]. FTIR spectra of synthesized nanocomposite PVA-Fe2O3 and PVA-Fe2O3-TiO2, recorded in the range of 400–4000cm−1 are shown in the Fig.2 b,c. The peak patterns of PVA-Fe2O3 appeared in the regions of 577cm−1 , 1640 cm−1 and 3247cm−1 corresponds to Fe-O, PVA with Fe . in the case of PVA-Fe2O3-TiO2 there are shifting in the wavenumber in reduction in the intensity of peaks [23]. The reduction in the intensity of all the peaks was observed in case of composites after the incorporation of TiO2.



(a)



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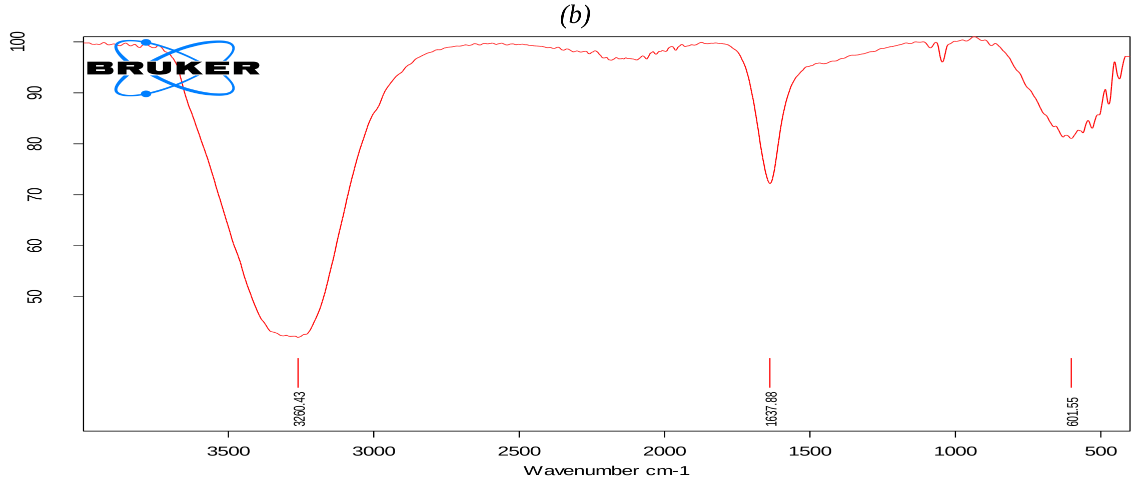

(c)

Fig. 2. FTIR spectra of (a) PVA-Fe2O3 (b) PVA-Fe2O3 with 2.5% TiO2 (c) PVA-Fe2O3 with 5 % TiO2.

Figure 3. shows the XRD Curve of PVA-Fe2O3 and PVA-TiO2. The XRD pattern shows that the as-fabricated products belong to the crystal phase of hematite Fe2O3 (JCPDS No. 1-1053) [24]. the diffraction peaks corresponding to Fe2O3 can be seen clearly. the two diffraction peaks position of Fe2O3 at 2θ = 33.50◦ and at 2 θ = 38.0◦ are confirm the formation of Fe2O3 [25-27].

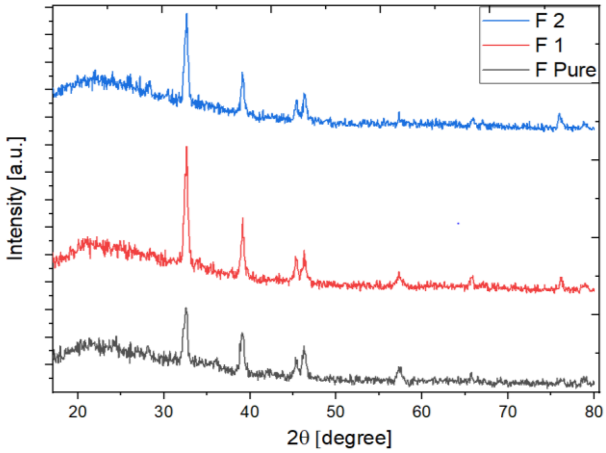

Fig. 3. XRD Curve of PVA-Fe2O3 and PVA-TiO2.

As seen in the Fig.4, PVA-Fe2O3 is highly transparent with transmittance of around 85 % in range 600-800 nm. After addition of 2.5 % by weight of TiO2 nanoparticles, the transmittance of nanocomposite drops to 75% in the same range of wavelength . Further addition of nanoparticles reduced the percentage transmittance to 68%.

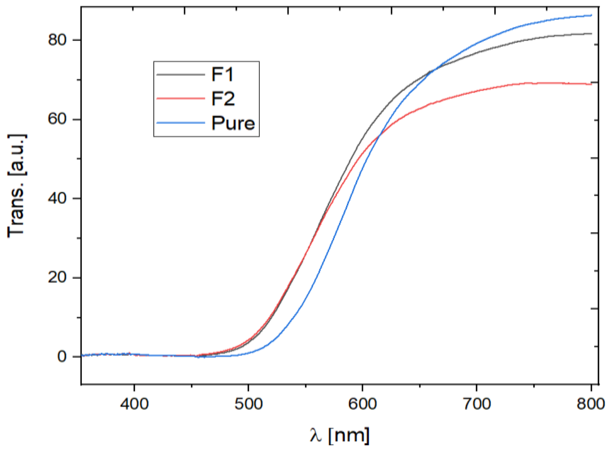

Fig. 4.UV-Visble transmision spectra of PVA-Fe2O3 PVA-Fe2O3-TiO2 composites.

The optical absorption spectra of the PVA-Fe2O3 and PVA-Fe2O3-TiO2 are presented in Fig. 5. The produced hybrids display strong absorption in the range of 440–570 nm. . It is important to note that the absorption peaks of the materials gradually move to shorter wavelengths with the addition of TiO2.

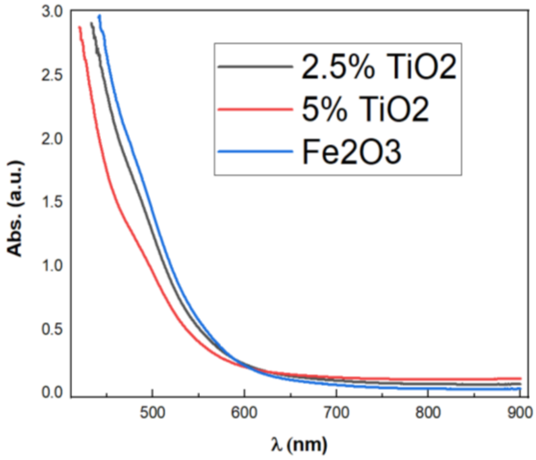

Fig. 5.UV-Visble absorption spectrums of PVA-Fe2O3 PVA-Fe2O3-TiO2 composites.

The band gap value of the synthesized iron oxide nanoparticles is 2.2 which is higher than that of bulk Fe2O3 [28] for which E_g value is 2.1 eV. Band gap widening is a striking effect of quantum confinement that has been observed in numerous other semiconductor materials possessing delocalized electronic states close to the Fermi level [29]. For structure contain TiO2 there are increase in the values of two ratio where it equal to 2.26 For 2.5 % and 2.4 eV. for 5 % content as shown if figure 6 [30].

Figure 7 shows the relationship between the TiO2 content in the composite with the energy band gaps. From figure can be found there are increasing in the value of energy gaps for with increasing of TiO2 ratio and this result has good agreement with references [30].

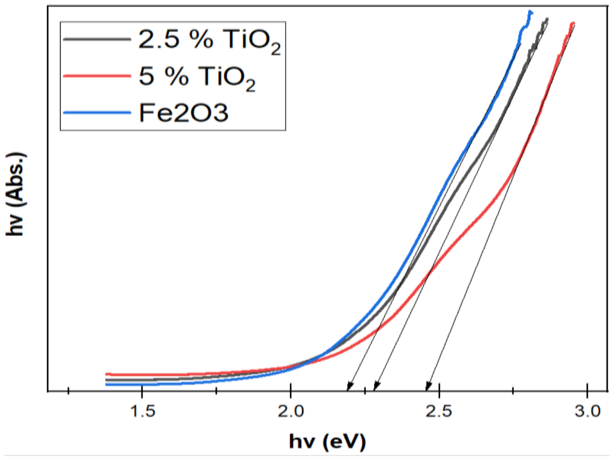

Fig. 6. Optical band gap of PVA-Fe2O3 PVA-Fe2O3-TiO2 composites.

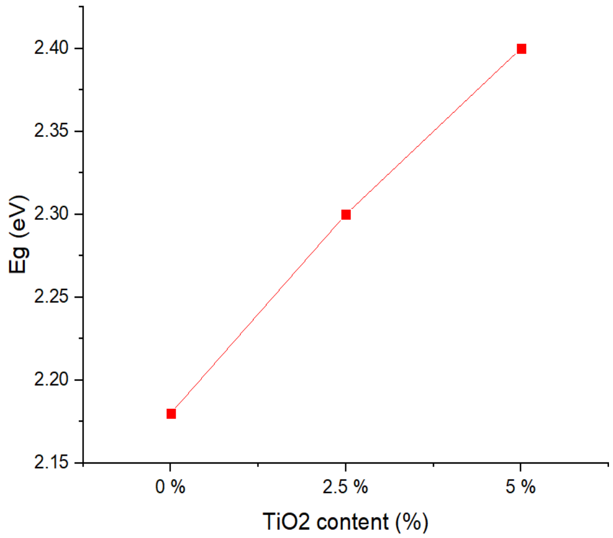

Fig. 7. The relationship between the TiO2 content in the composite with the energy band gaps.

4. Conclusions

In the present work, PVA and Fe2O3 nanoparticles were prepared by chemical method. The effect of addition of TiO2 with two ratios on optical, structural and morphological properties have been tested by FTIR,UV-VIS,XRD and FESEM. FTIR spectra analyses confirmed the incorporation of NP in polymer matrix. With the addition of 2.5 % TiO2 nanoparticles, the transmittance of nanocomposite decreased by 10 % whereas after further addition in steps of 5% NP the transmittance decreased by 18 %. One of the remarkable properties of PVA/ Fe2O3 nanocomposites was the change in the optical band gap with addition of NP. The optical band gap of nanocomposite increased with the increase of nanoparticles concentration.

References

[1] Shubayev, V. I., Pisanic II, T. R., & Jin, S., Adv. Drug Delivery Rev. 61(6), 467-477 (2009); https://doi.org/10.1016/j.addr.2009.03.007

[2] D. Patel, J.Y. Moon, Y. Chang, T.J. Kim, G.H. Lee, Colloid Surf. A 313-314, 91 (2008); https://doi.org/10.1016/j.colsurfa.2007.04.078

[3] M. Zhao, L. Josephson, Y. Tang, R. Weissleder, Angew. Chem. Int. Ed. 42, 1375 (2003); https://doi.org/10.1002/anie.200390352

[4] S. Mornet, S. Vasseur, F. Grasset, P. Veverka, G. Goglio, A. Demourgues et al., Prog. Solid State Chem. 34, 237 (2006); https://doi.org/10.1016/j.progsolidstchem.2005.11.010

[5] P.D. Stevens, J. Fan, H.M.R. Gardimalla, M. Yen, Y. Gao, Org. Lett. 7, 2085 (2005); https://doi.org/10.1021/ol050218w

[6] Y. Jun, J. Choi, J. Cheon. Chem. Commun. (Camb) 1203 (2007); https://doi.org/10.1039/B614735F

[7] Ahilfi, D. N., Alkabbi, A. S., Mohammed, K. A., & Ziadan, K. M. (2020, November). Fabrication and Characterization of polyaniline/CdSe Device for Applications in Nano Structured Solar Cells. In IOP Conference Series: Materials Science and Engineering (Vol. 928, No. 7, p. 072069). IOP Publishing; https://doi.org/10.1088/1757-899X/928/7/072069

[8] K. A. Mohammed , Shireen N. Alebadi , K. M. Ziadan, A. S. AL-Kabbi ,A. J. Alrubaie, Hussein M. Hussein (2022) "Organic-inorganic hybrid material: synthesis, characterization for solar cell application" Journal of Ovonic Research Vol. 18, No. 1, January - February 2022; https://doi.org/10.15251/JOR.2022.181.75

[9] Kahtan A. Mohammed, Kareema M. Ziadan, Alaa S. AL-Kabbi, Rahman S. Zbibah, Ali Jawad Alrubaie, (2022), "Conducting polymer/CdSe hybrid as bulk heterojunction solar cell" Acta Physica Polonica A, Vol 141, No. 3; https://doi.org/10.12693/APhysPolA.141.198

[10] Mohammed, K. A., Abdulridha, S. A., Aljbory, E. H., Alkhayatt, A. H. O., Zbibah, R. S., Alrubaie, A. J., ... & Kadhem, M. J. (2021). Capping agent effect on optical properties of Fe2O3 nanoparticles. Materials Today: Proceedings; https://doi.org/10.1016/j.matpr.2021.11.346

[11] S. Srivastava, M. Haridas, J.K. Basu, Optical Properties of Polymer Nanocomposites, vol. 31, (2008), pp. 213-217; https://doi.org/10.1007/s12034-008-0038-9

[12] A.A. Ebnalwaled, A. Thabet, Controlling the optical constants of PVC nanocomposite films for optoelectronic applications, Synth. Met. 220 (2016) 374-383; https://doi.org/10.1016/j.synthmet.2016.07.006

[13] S.B. Aziz, H.M. Ahmed, A.M. Hussein, A.B. Fathulla, R.M. Wsw, R.T. Hussein, Tuning the absorption of ultraviolet spectra and optical parameters of aluminum doped PVA based solid polymer composites, J. Mater. Sci. Mater. Electron. 26 (2015) 8022-8028; https://doi.org/10.1007/s10854-015-3457-6

[14] T. Saleh, A. Kösemen, S.E. San, M.K. El Mansy, Preparation and characterization of CuI / PVA - PEDOT : PSS core - shell for photovoltaic application, Opt. Int. J. Light Electron Opt. 125 (2014) 2009-2016; https://doi.org/10.1016/j.ijleo.2013.03.175

[15] M.H. Makled, E. Sheha, T.S. Shanap, M.K. El-Mansy, Electrical conduction and dielectric relaxation in p-type PVA/CuI polymer composite, J. Adv. Res. 4 (2013) 531-538; https://doi.org/10.1016/j.jare.2012.09.007

[16] E. Sheha, H. Khoder, T.S. Shanap, M.G. El-Shaarawy, M.K. El Mansy, Structure, dielectric and optical properties of p-type (PVA/CuI) nanocomposite polymer electrolyte for photovoltaic cells, Optik (Stuttg) 123 (2012); https://doi.org/10.1016/j.ijleo.2011.06.066

[17] Sangaiya, P., & Jayaprakash, R. (2018). A review on iron oxide nanoparticles and their biomedical applications. Journal of Superconductivity and Novel Magnetism, 31(11), 3397-3413; https://doi.org/10.1007/s10948-018-4841-2

[18] Schwertmann, U., & Cornell, R. M. (1996). The iron oxides: structure, properties, reactions, occurrence and uses. VCH Verlag, Weinheim.

[19] Vayssieres, L., Sathe, C., Butorin, S.M., Smith, D.K., Nordgren, J., Guo, J.H.: Adv. Mater. 17, 2320-2323 (2005); https://doi.org/10.1002/adma.200500992

[20] Arias, L. S., Pessan, J. P., Vieira, A. P. M., Lima, T. M. T. D., Delbem, A. C. B., & Monteiro, D. R. (2018). Iron oxide nanoparticles for biomedical applications: a perspective on synthesis, drugs, antimicrobial activity, and toxicity. Antibiotics, 7(2), 46; https://doi.org/10.3390/antibiotics7020046

[21] Vasile, E., Sima, M., Sima, A., & Logofatu, C. (2020). TiO2/Fe2O3 photoanodes for solar water oxidation prepared via electrodeposition of amorphous precursors. Materials Research Bulletin, 121, 110623; https://doi.org/10.1016/j.materresbull.2019.110623

[22]X.N. Xu, Y. Wolfus, A. Shaulov, Y. Yeshurun, I. Felner, I. Nowik, Y. Koltypin, A. Gedanken Annealing study of Fe2O3 nanoparticles: magnetic size effects and phase transformations J. Appl. Phys., 91 (2002), pp. 4611-4616; https://doi.org/10.1063/1.1457544

[23] Li, X., Yu, J. & Jaroniec, M. Chem Soc Rev Hierarchical photocatalysts. Chem. Soc. Rev. 45, 2603-2636 (2016); https://doi.org/10.1039/C5CS00838G

[24] Cheng, G., Xu, F., Xiong, J., Wei, Y., Stadler, F. J., & Chen, R. (2017). A novel protocol to design TiO2-Fe2O3 hybrids with effective charge separation efficiency for improved photocatalysis. Advanced Powder Technology, 28(2), 665-670; https://doi.org/10.1016/j.apt.2016.12.004

[25] Mei, Q., Zhang, F., Wang, N., Yang, Y., Wu, R., & Wang, W. (2019). TiO 2/Fe 2 O 3 heterostructures with enhanced photocatalytic reduction of Cr (vi) under visible light irradiation. RSC advances, 9(39), 22764-22771; https://doi.org/10.1039/C9RA03531A

[26] Mirmasoomi, S. R., Ghazi, M. M., & Galedari, M. (2017). Photocatalytic degradation of diazinon under visible light using TiO2/Fe2O3 nanocomposite synthesized by ultrasonic-assisted

impregnation method. Separation and Purification Technology, 175, 418-427; https://doi.org/10.1016/j.seppur.2016.11.021

[27] Bepari, R. A., Bharali, P., & Das, B. K. (2017). Controlled synthesis of α-and γ-Fe_2O_3 nanoparticles via thermolysis of PVA gels and studies on α-Fe_2O_3 catalyzed styrene epoxidation. Journal of Saudi Chemical Society, 21, S170-S178; https://doi.org/10.1016/j.jscs.2013.12.010

[28] Brus, L. E. (1984). Electron-electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state. The Journal of chemical physics, 80(9), 4403-4409; https://doi.org/10.1063/1.447218

[29] Wen, X., Wang, S., Ding, Y., Wang, Z. L., & Yang, S. (2005). Controlled growth of large-area, uniform, vertically aligned arrays of α-Fe_2O_3 nanobelts and nanowires. The Journal of Physical Chemistry B, 109(1), 215-220; https://doi.org/10.1021/jp0461448

[30] Koohestani, H. (2019). Synthesis and characterisation of TiO_2 nanoparticles/Fe_2O_3 waste chips composite. Micro & Nano Letters, 14(6), 678-682; https://doi.org/10.1049/mnl.2018.5583