Digest Journal of Nanomaterials and Biostructures Vol. 18, No. 4, October-December 2023, p.1315-1325

# Influence of the isothermal annealing time on structural morphological, and photocatalytic characters of BiT/ZnWO<sub>4</sub> composite

# H. Menasra<sup>\*</sup>, Z. Necira, K. Bounab, C. Benbrika, L. Smaili Laboratory of Applied Chemistry, Departement of Science of Matter, University of Biskra, BP 145 RP, Biskra 07000, Algeria.

The abbreviated composite  $Bi_4Ti_3O_{12}/ZnWO_4$  (BIT/ZW) was produced using the molten salt technique at 800°C. The impact of isothermal annealing time, in the second step, on the structural, morphological, and photocatalytic properties was investigated. X-ray diffraction (XRD) confirmed the formation of composites with varying proportions (76.8% BIT, 20.2% ZW), (71% BIT, 22.8% ZW), and (56.4% BIT, 36.6% ZW) at annealing times of 4, 6, and 8 hours at 950°C, respectively. A minor amount of pyrochlore phases (<7%) was observed. Increasing the annealing time affected the crystallinity of the composites. The crystallite size and grain size of BIT and ZnWO<sub>4</sub> decreased with longer annealing times, leading to a reduction in the band gap from 2.95 to 2.83 eV. The composite (76.8% BIT, 20.2% ZW) exhibited photocatalytic activity that was two times higher for degrading methylene blue (MB) in the dark compared to the other composites, but showed an improvement in degradation under solar irradiation from 70% to 72.18%. The results indicate that annealing isothermal time can effectively modify the properties of the composites, creating a proven heterojunction between BIT and ZnWO<sub>4</sub>.

(Received August 3, 2023; Accepted October 26, 2023)

*Keywords:* Photocatalyst, Aurivillius BIT, ZnWO<sub>4</sub>, Composite, Methylene blue degradation.

### 1. Introduction

Over the past few years, researchers have been confronted with a substantial obstacle in tackling the crisis of water pollution caused by human activities. This pollution not only endangers human health but also poses a threat to the environment [1-3]. Among the various technologies available, photocatalytic technology utilizing environmentally friendly semiconductors has emerged as the most promising solution to combat pollution caused by heavy metals [1-3], inorganic pollutants [4-7], organic pollutants [8-11], and even bacteria[12].

Zinc tungstate wolframite, represented by the general formula ZnWO<sub>4</sub>, is a semiconductor with a monoclinic structure at room temperature and remarkable photocatalytic properties. These properties are closely associated with its energy bandgap, which varies between 3.05 and 4.7 eV [13-18]. The diverse range of values can be attributed to differences in synthesis methods, which affect factors such as crystallite size[19], morphology[20], and specific surface area[21]. Various methods have been proposed in the literature to enhance the photocatalytic properties of ZnWO<sub>4</sub>. For instance, L.N.M. Araújo et al. [22] reported that by modifying the synthesis conditions, such as annealing temperature ranging from 400°C to 800°C in 50°C increments, the bandgap energy can be reduced from 3.97 eV to 3.2 eV. Similarly, V. Faka et al. [23] obtained a slightly lower bandgap energy (3.1 eV) at an optimum temperature of 600°C. Another approach to improve catalytic properties involves the creation of heterojunctions with materials such as graphene [24-26], metals [11, 27, 28], simple oxides [29-32], or complex oxides such as spinel [33-37], perovskite [38], and Aurivillius double-layered structures [16, 18, 39, 40]. These heterojunctions have demonstrated the capability to degrade over 80% of cationic or anionic dyes.

The objective of this study is to explore new composite materials based on ZnWO<sub>4</sub> that could be competitive for potential photocatalytic applications. To achieve this, we have chosen to

<sup>\*</sup> Corresponding author: h.menasra@univ-biskra.dz

https://doi.org/10.15251/DJNB.2023.184.1315

synthesize a molten salt mixture of Aurivillius  $Bi_4Ti_3O_{12}$  and  $ZnWO_4$ , with variations in the sintering time. The aim is to investigate the effect of isothermal treatment time on the phase ratio (BIT and  $ZnWO_4$ ) of the composite and to study the photocatalytic properties of the resulting compounds on the sunlight degradation of pollutant methylene blue.

# 2. Experimental procedure

#### 2.1. Catalyst preparation

It is well known that synthesis parameters such as precursor selection, calcination and sintering time, heating and cooling rate, pH, and concentration play a crucial role in determining the size, shape, and surface properties of nanomaterials [40-42]. Therefore, we chose the molten salt method to synthesize the  $Bi_4Ti_3O_{12}/ZnWO_4$  composite, abbreviated as BIT-ZW. Stoichiometric amounts of high-purity precursors of the BIT compound,  $Bi_2O_3$  (99.9%) and  $TiO_2$  (99.9%), were mixed with a (1:1) ratio of (NaCl : KCl) for 4 hours. The reaction mixture was calcined at 800°C for 4 hours with a heating rate of (2°C/min). Subsequently, the calcined mixture was ground with stoichiometric amounts of ZnO (99.5%) and WO<sub>3</sub> (99.9%) for 4 hours. The resulting powder was then subjected to a second calcination at 950°C for 4, 6, and 8 hours, with the same heating rate of (2°C/min). The material was washed multiple times with hot water until the chlorinated salts were completely removed.

After drying at 80°C for 12 hours, the structural analysis was performed using X-ray diffraction (XRD), morphological analysis was conducted using scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR), and the degradation kinetics of methylene blue under sunlight irradiation was studied using UV-visible spectroscopy.

#### 2.2. Photocatalytic test

In all photocatalytic activity experiments, catalysts (100 mg) were placed in a solution of MB dye (100 ml, 1 mg.l<sup>-1</sup>, normal pH = 6.04) under solar irradiation in the month of June in the Biskra region (Algeria), while maintaining a temperature of 25 °C using a closed water circuit. The dye was analyzed using a UV-vis-NIR spectrophotometer (Perkin-Elmer, Lambda 850) at  $\lambda$ = 664 nm. At 15-minute intervals of solar irradiation, samples (4 mL) of the reaction solution were taken, centrifuged, and filtered. Finally, the filtrates were analyzed. The degradation efficiency was calculated using following equation (1):

$$R_{MB}(\%) = (C_0 - C_t)/C_0 \times 100\%$$
(1)

where ;  $C_0$  (mg/l) represents the initial concentration of MB, and  $C_t$  (mg/l) is the concentration of the collected quantities after centrifugation.

The Scheme 1 illustrates the stepwise preparation and characterization of a composite photocatalyst under the effect of isothermal time annealing.



Scheme 1. Stepwise illustration of Molten-salts reaction of (BIT/ZW) under the effect of isothermal time annealing.

## 3. Results and discussions

#### 3.1. XRD analysis

Fig. 1 illustrates the results of the X-ray diffraction (XRD) spectral analysis of the samples after thermal treatment. Firstly, the peaks of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> were indexed to the BIT prototype lattice (ICSD No. 98-002-4738), indicating an orthorhombic structure with the Fmmm space group. The lattice parameters for pure Aurivillius BIT were calculated using HighScore Plus software, resulting in a = 5.402 Å, b = 5.454 Å, c = 32.594 Å,  $\alpha = \beta = \gamma = 90^{\circ}$ . The crystallite size, determined by the D. Scherrer method using the highest peak of the three-layer Aurivillius[43], the (hkl) plane (117), is in the nanometer range (41.23 nm) (Table 1).



*Fig. 1. X-ray diffraction patterns of BIT pur, and (x% BIT, y% ZW) composites at time 4, 6 and 8 Hrs isotherme (950°C) traitement.* 

### 1318

The addition of one mole of zinc oxide and tungsten, followed by recalcination at 950°C for 4 hours, 6 hours, and 8 hours, resulted in a composite (x% BIT, y% ZW) with varying proportions : (76.8% BIT, 20.2% ZW), (71.2% BIT, 8% ZW), and (56.4% BIT, 36.6% ZW). All the peaks of the ZnWO<sub>4</sub> compound can be attributed to the monoclinic crystal structure of the card (ICSD no. 98-016-9214) with a space group of P12/C1. A minor amount of pyrochlore, approximately 3%, was observed to form through the reaction  $Bi_2O_3 + 2 TiO_2 \rightarrow Bi_2Ti_2O_7$  at 4 hours in 950°C. However, this phase increased to 7% with a decrease in the BIT phases, indicating the instability of the Aurivillius phase with a change in the isothermal processing time. This resulted in the formation of the pyrochlore phase through the reaction:  $Bi_4Ti_3O_{12} \rightarrow Bi_2Ti_2O_7 + Bi_2O_3 + TiO_2$ . Therefore, since the secondary phase does not exceed 7%, the formed composites can be considered biphasic [44].

#### 3.2. FTIR analysis

Fig. 2 shows the FTIR spectrum of the (x% BIT- y% ZW) samples sintered at 950°C. The (x% BIT - y% ZW) composites are a two-phase mixture consisting of an Aurivillius BIT three-layer phase and ZnWO<sub>4</sub> wolframite phase. Most of the vibrations of the considered bonds are consecutive in nature. A wide band observed at [583-663] cm<sup>-1</sup> corresponds to the vibration of the oxygen atoms in the octahedron [TiO<sub>6</sub>]<sub>6</sub> of Aurivillius BIT [45-47]. The bands at 820 and 880 cm<sup>-1</sup> are associated to the vibration of the W-O bonds, while the bands at 600 and 700 cm<sup>-1</sup> are attributed to the Zn-O-W bonds of ZnWO<sub>4</sub> [48, 49]. Additionally, the band at 1600 cm<sup>-1</sup> is linked to the presence of absorbed water in the composite or the KBr used to dilute the samples in the analyte pellets[48].



Fig. 2. FTIR spectrum of (x% BIT-y% ZW) composites at time 4, 6 and 8hrs isotherme (950°C) traitement.

### 3.3. SEM/X-EDX analysis

The analysis of the samples using scanning electron microscopy (SEM) of the solid solution allowed for determining the surface condition of the different samples. This technique provides an estimation of grain distribution and average grain size after sintering at 950°C [50-52]. The micrographs of the composites in Fig. 3 (a, b, and c), at a scale of 20  $\mu$ m, confirm the formation of two phases, one appearing as plates (BIT) and the other as spheres (ZW), while the pyrochlore phase exhibits a pyramidal shape. The three histograms in Fig. 3 (d, e, and f) show a slight variation in the average grain size of the ZnWO<sub>4</sub> compound with changes in the holding time at 950°C, ranging from 1.87 to 1.6  $\mu$ m. On the other hand, the BIT grains have a plate-shaped

form with a slight decrease in size. The following table 1 presents the results of calculating the average grain size obtained using « image J » analysis software.

	Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>			ZnWO <sub>4</sub>			
	Deby scherrer	SEM analysis		Deby	scherrer	SEM analysis (µm)	
	(117) (Å)	Width (µm)	Thickness (µm)	(111)(Å)			
4 Hrs	561.17	17.5	0.702	549.02		1.87	
6 Hrs	696.47	9.84	0.6	479.32		1.8	
8 Hrs	933 73	6.03	0 401	461 2		16	

Table 1. Crystallite and grain size characteristics of (BIT/ZW) composite during different times(4, 6, and 8 hours) at isothermal 950°C.



Fig. 3. (a- c) SEM images of (x% BIT- y% ZW) composites (20 $\mu$ m scale), (d- f) Histograms grain size of ZnWO<sub>4</sub> in the composites.

The X-EDS analysis was conducted concurrently with SEM analysis on the surfaces of the sintered samples to obtain comprehensive insights. The X-EDS spectrum presented in Figure 4(a-d) illustrates the elemental composition of the (x% BT-y% ZW) samples sintered at 950°C. The spectrum confirms the presence of all constituent elements of the biphasic compound, including Bismuth (Bi), Tungsten (W), Titanium (Ti), Zinc (Zn), and oxygen (O).



Fig. 4. (a- b) X-EDS spectra obtained on the BIT-ZW sample recalcined at 950 °C during different times (4, 6, and 8 hours).

# 3.4. Photocatalytic study

Since the discovery of Aurivillius  $Bi_4Ti_3O_{12}$  and  $ZnWO_4$ , they have been considered as powerful photocatalysts due to their ability to rapidly decompose and mineralize a wide range of natural organic matter and organic pollutants, attributed to their narrow band gaps ranging from 2.7 to 3.2 eV [53-55] and 3.05 to 4.7 eV [14-18], respectively. We utilized the direct transition model proposed by Wood and Tauc [56-58] to determine the optical band gap of the sintered (x% BIT-y% ZW) composites at 950°C. This was accomplished by plotting the absorbance curve (fig. 5(a)) and ( $\alpha$ hv)<sup>2</sup> versus (hv) (fig. 5(b)). By extrapolating a linear fit to the plot to zero in Fig. 5(b), we obtained estimated energy gaps of 2.95, 2.89, and 2.83 eV. There is a slight decrease in the band gap energy values due to changes in crystallite size and scattering phenomena[59], indicating the presence of a heterojunction between Aurivillius and ZnWO<sub>4</sub>.



Fig. 5. (a) UV-vis absorbance spectra (b) Fitting plots of  $(\alpha h v)^2$  versus (hv) in terms of Wood and Tauc model of (x% BIT, y% ZW) composites.

Fig. 6 (a, b) shows the efficiency of methylene blue (MB) photodegradation under solar irradiation using the composite catalyst (x% BIT, y% ZW). It was observed that the catalysts (76.8% BIT, 20.2% ZW), (71.3% BIT, 22.8% ZW), and (56.4% BIT, 36.6% ZW) successively degraded methylene blue by 57.47%, 32.28%, and 24.43% after 30 minutes of dark adsorption, and 70.35%, 72.15%, and 70.18% after 75 minutes of photocatalysis under solar irradiation.

In most cases, the degradation kinetics of many organic molecules are described as a firstorder reaction following the Langmuir-Hinshelwood kinetic model at low concentration [60]. Therefore, according to the following equation (2):

$$V = -dC/dt = k_{app.} \times C$$
<sup>(2)</sup>

where V is the photocatalytic degradation rate (mg·l<sup>-1</sup>·min),  $k_{app.}$  is the apparent degradation constant (min<sup>-1</sup>), C is the concentration of MB dye in solution (mg·l<sup>-1</sup>), and t is the irradiation time (min). Integrating equation (2) (with the initial condition:  $C = C_0$  at t = 0) leads to the following Equation(3):

$$Ln(C_0/C_t) = k_{app.} \times t$$
(3)

The regression coefficient and the kinetic constant were estimated by linear fitting of  $Ln(C_t/C_0)$  versus t (Fig. 4 (c, d, e)) and listed in Table 2. This implies that the half-life of dye degradation will occur at  $t_{1/2} = 0.693/k_{app.}$  at 74, 78, and 96 min.

Based on the analysis results, which are consistent with previous studies on composite semiconductor nanoparticles based on BIT or ZnWO<sub>4</sub> [19, 49, 51, 53, 55, 61], we propose a possible photocatalytic mechanism illustrated in Fig. 6(f), confirming that photon absorption allows for the excitation of  $e^-$  to the highest conduction band (CB) of BIT to the lower (CB) of ZnWO<sub>4</sub>, resulting in the generation of oxidizing or reducing species on the semiconductor surface. These species, mostly highly oxidizing 'OH radicals, are formed near the catalyst from water and oxygen in the air. They attack the chemical bonds of most organic compounds (pollutants) and partially or completely destroy them. The short half-life of the radicals prevents them from being transported far from the active surface [61].

The values of the conduction band (CB) and valence band (VB) potentials of BIT and ZnWO<sub>4</sub> were calculated using the following equations (4 and 5) [61, 62]:

$$E_{\rm VB} = \chi - E_e + E_g/2 \tag{4}$$

$$E_{CB} = E_{VB} - E_g \tag{5}$$

where  $\chi$  is the absolute electronegativity of the semiconductor,  $E_e$  is the energy of free electrons on the hydrogen scale (approximately 4.5 eV), and Eg is the experimental energy of the band gap for BIT (2.86 eV) and ZnWO<sub>4</sub> (3.25 eV).

Table 2. Photocatalytic characteristics and kinetics of MB dye degradation in the presence of catalysts (x%BIT, y% ZW) under solar irradiation.

Composite	R% in dark	R% in Sunleight	$K_{app} / R^2$	t <sub>1/2</sub> (min)	Eg (eV)
(x% BIT, y% ZW)					
BIT					2.86
ZnWO <sub>4</sub>					3.25
(76.8 BIT, 20.2 ZW)	57.47	70.35	0.00928/ 0.987	74	2.95
(71.3 BIT, 22.8 ZW)	32.28	72.15	0.00879/ 0.986	78	2.89
(56.4 BIT, 36.6 ZW)	24.43	72.18	0.00721/ 0.99	96	2.83

1322



Fig. 6. (a, b) Photocatalytic degradation efficiency curves of MB under solar irradiation in the presence of the photocatalyst (x% BIT/y% ZW); (c-e) first-order kinetic curves of the three composites; (f) proposed mechanism for MB degradation.

# 4. Conclusion

In summary,  $Bi_4Ti_3O_{12}/ZnWO_4$  composites were successfully synthesized using the molten salt method, followed by an isothermal treatment at 950°C for 4, 6, and 8 hours. X-ray diffraction (XRD) analysis and the ICSD data of the pure synthesized  $Bi_4Ti_3O_{12}$  (BIT) using the same method indicated the formation of composites (x% BIT, y% ZW%) with varying proportions, along with a minor pyrochlore phase below 7%. Furthermore, FT-IR spectroscopy confirmed these structures as most of the considered bond vibrations were detected. The UV-Vis spectra revealed a decrease in the Eg values with increasing isothermal treatment time. The photocatalytic performance for the degradation of the MB dye was studied for all composites, and the results confirm that it is influenced by changes in the isothermal time at 950°C.

# Acknowledgements

The authors would like to thank Ms. Soltani Mohamed Toufik of the Laboratory of Photonic Physics and Multifunctional Nanomaterials, Biskra University, for her help with the FTIR and UV-visible measurements. We would also like to thank Ms. Soumia Khelifa from the Chemistry Laboratory for her valuable assistance in completing this work at the educational chemistry laboratory.

# References

[1] S.S. Alelyani, Y.N. Kavil, R.K. Al-Farawati, M. Zobidi, M.A. Salam, Y.A. Shaban, Research on Chemical Intermediates 49 (2023) 1819-1842 ; <u>https://doi.org/10.1007/s11164-023-04983-y</u>

[2] Y. Guo, Y. Yang, X. Yin, J. Zhao, Y. Han, J. Liu, W. Chen, M. Que, J. Zhang, W. Que, Journal of Alloys and Compounds 774 (2019) 75-81;

https://doi.org/10.1016/j.jallcom.2018.09.097

[3] D. Saini, J. Kaushik, A.K. Garg, C. Dalal, S.K. Sonkar, ACS Applied Bio Materials 3 (2020) 3656-3663 ; https://doi.org/10.1021/acsabm.0c00296

[4] T. Tatarchuk, M. Bououdina, B. Al-Najar, R.B. Bitra, A new generation material graphene: Applications in water technology (2019) 69-110 ; <u>https://doi.org/10.1007/978-3-319-75484-0\_4</u>

[5] R. Yang, S. Zhong, L. Zhang, B. Liu, Separation and Purification Technology 235 (2020) 116270 ; <u>https://doi.org/10.1016/j.seppur.2019.116270</u>

[6] A. Talaiekhozani, S. Rezania, K.-H. Kim, R. Sanaye, A.M. Amani, Journal of Cleaner Production 278 (2021) 123895 ; <u>https://doi.org/10.1016/j.jclepro.2020.123895</u>

[7] G. Huang, C. Zhang, Y. Zhu, Journal of Alloys and Compounds 432 (2007) 269-276 ; https://doi.org/10.1016/j.jallcom.2006.05.109

[8] M. Umar, H.A. Aziz, Organic pollutants-monitoring, risk and treatment 8 (2013) 196-197.

[9] C.-C. Wang, J.-R. Li, X.-L. Lv, Y.-Q. Zhang, G. Guo, Energy & Environmental Science 7 (2014) 2831-2867 ; <u>https://doi.org/10.1039/C4EE01299B</u>

[10] B. Bathula, S.B. Eadi, H.-D. Lee, K. Yoo, Environmental Research 228 (2023) 115851 ; https://doi.org/10.1016/j.envres.2023.115851

[11] J. Zhang, X. Sun, J. Ma, Z. Yi, T. Xian, S. Wang, G. Liu, X. Wang, H. Yang, Applied Surface Science 611 (2023) 155681 ; <u>https://doi.org/10.1016/j.apsusc.2022.155681</u>

[12] H. He, Z. Luo, C. Yu, Journal of Photochemistry and Photobiology A: Chemistry 401 (2020) 112735 ; <u>https://doi.org/10.1016/j.jphotochem.2020.112735</u>

[13] N. Pavithra, G. Nagaraju, S. Patil, Ionics 27 (2021) 3533-3541; https://doi.org/10.1007/s11581-021-04123-9

[14] M. Mosleh, K. Taherinejat, Journal of Materials Science: Materials in Electronics 27 (2016) 10510-10515; <u>https://doi.org/10.1007/s10854-016-5141-x</u>

[15] F.A. Alharthi, W.S. Al-Nafaei, A.A. Alshayiqi, H.S. Alanazi, I. Hasan, Catalysts 13 (2023) 404 ; https://doi.org/10.3390/catal13020404

[16] B. Babu, R. Koutavarapu, J. Shim, K. Yoo, Journal of the Taiwan Institute of Chemical Engineers 110 (2020) 58-70 ; <u>https://doi.org/10.1016/j.jtice.2020.03.011</u>

[17] V. Pavitra, B. Praveen, G. Nagaraju, Materials Chemistry and Physics 293 (2023) 126882 ; https://doi.org/10.1016/j.matchemphys.2022.126882

[18] P. Kumar, S. Verma, N.Č. Korošin, B. Žener, U.L. Štangar, Catalysis Today 397 (2022) 278-285 ; <u>https://doi.org/10.1016/j.cattod.2021.09.012</u>

[19] Q. Wu, X. Liu, S. Hou, L. Qiang, K. Zhang, Z. Yang, Colloids and Surfaces A: Physicochemical and Engineering Aspects 629 (2021) 127459 ; https://doi.org/10.1016/j.colsurfa.2021.127459

[20] Z. Amouzegar, R. Naghizadeh, H. Rezaie, M. Ghahari, M. Aminzare, Ceramics International 41 (2015) 8352-8359 ; <u>https://doi.org/10.1016/j.ceramint.2015.03.020</u>

1324

[21] Y. Li, F. Zhou, Applied Surface Science 496 (2019) 143645; https://doi.org/10.1016/j.apsusc.2019.143645

[22] L. de Araújo, B. Sousa, A. de Araújo, R. Monção, M. Feitor, J. Sczancoski, M. Almeida, F. Santos, R. de Sousa, L. Cavalcante, Journal of materials science (2023) 1-28.

[23] V. Faka, S. Tsoumachidou, M. Moschogiannaki, G. Kiriakidis, I. Poulios, V. Binas, Journal of Photochemistry and Photobiology A: Chemistry 406 (2021) 113002 ; https://doi.org/10.1016/j.jphotochem.2020.113002

[24] X. Bai, L. Wang, Y. Zhu, ACS Catalysis 2 (2012) 2769-2778 ; https://doi.org/10.1021/cs3005852

[25] W. Wang, J. Shen, N. Li, M. Ye, Materials Letters 106 (2013) 284-286 ; https://doi.org/10.1016/j.matlet.2013.05.042

[26] K. Qureshi, M.Z. Ahmad, I.A. Bhatti, M. Zahid, J. Nisar, M. Iqbal, Journal of Molecular Liquids 285 (2019) 778-789 ; <u>https://doi.org/10.1016/j.molliq.2019.04.139</u>

[27] J. Ke, C. Niu, J. Zhang, G. Zeng, Journal of Molecular Catalysis A: Chemical 395 (2014) 276-282 ; <u>https://doi.org/10.1016/j.molcata.2014.08.039</u>

[28] C. Yu, C.Y. Jimmy, Materials Science and Engineering: B 164 (2009) 16-22 ; https://doi.org/10.1016/j.mseb.2009.06.008

[29] M. Emsaki, S. Hassanzadeh-Tabrizi, A. Saffar-Teluri, Journal of Materials Science: Materials in Electronics 29 (2018) 2384-2391 ; <u>https://doi.org/10.1007/s10854-017-8157-y</u>

[30] A. Somdee, S. Wannapop, Colloid and Interface Science Communications 47 (2022) 100591 ; https://doi.org/10.1016/j.colcom.2022.100591

[31] C. Jaramillo-Páez, J. Navío, F. Puga, M. Hidalgo, Journal of Photochemistry and Photobiology A: Chemistry 404 (2021) 112962 ;

https://doi.org/10.1016/j.jphotochem.2020.112962

[32] G.M. Kumar, D. Lee, H. Jeon, P. Ilanchezhiyan, K.D. Young, K.T. Won, Ceramics International 48 (2022) 4332-4340 ; <u>https://doi.org/10.1016/j.ceramint.2021.10.228</u>

[33] C.V. Reddy, R. Koutavarapu, K.R. Reddy, N.P. Shetti, T.M. Aminabhavi, J. Shim, Journal of environmental management 268 (2020) 110677 ; <u>https://doi.org/10.1016/j.jenvman.2020.110677</u>

[34] S. Chandrasekaran, C. Bowen, P. Zhang, Z. Li, Q. Yuan, X. Ren, L. Deng, Journal of Materials Chemistry A 6 (2018) 11078-11104 ; <u>https://doi.org/10.1039/C8TA03669A</u>

[35] V. Dutta, S. Sharma, P. Raizada, A. Hosseini-Bandegharaei, V.K. Gupta, P. Singh, Journal of Saudi Chemical Society 23 (2019) 1119-1136 ; <u>https://doi.org/10.1016/j.jscs.2019.07.003</u>

[36] R. Koutavarapu, C.V. Reddy, K. Syed, K.R. Reddy, T.A. Saleh, D.-Y. Lee, J. Shim, T.M. Aminabhavi, Journal of Hazardous Materials 423 (2022) 127044 ; https://doi.org/10.1016/j.jhazmat.2021.127044

[37] M. Amin Marsooli, M. Rahimi Nasrabadi, M. Fasihi-Ramandi, K. Adib, S. Pourmasoud, F. Ahmadi, M. Eghbali, A. Sobhani Nasab, M. Tomczykowa, M.E. Plonska-Brzezinska, Catalysts 10 (2020) 494 ; <u>https://doi.org/10.3390/catal10050494</u>

[38] W. Guo, B. Zhao, L. Huang, Y. He, Materials Letters 277 (2020) 128327 ; https://doi.org/10.1016/j.matlet.2020.128327

[39] H. Jiang, J. He, C. Deng, X. Hong, B. Liang, Molecules 27 (2022) 8698 ; https://doi.org/10.3390/molecules27248698

[40] H. Wang, C. Xie, Journal of Physics and Chemistry of Solids 69 (2008) 2440-2444 ; https://doi.org/10.1016/j.jpcs.2008.04.036

[41] C.S. Chua, X. Fang, X. Chen, O.K. Tan, M.S. Tse, A.M. Soutar, X. Ding, Chemical Vapor Deposition 20 (2014) 44-50 ; <u>https://doi.org/10.1002/cvde.201207015</u>

[42] L. Munguti, F. Dejene, Nano-Structures & Nano-Objects 24 (2020) 100594 ; https://doi.org/10.1016/j.nanoso.2020.100594

[43] H. Menasra, K. Bounab, Z. Necira, A. Meklid, A. Boutarfaia, Int. J. Thin. Fil. Sci. Tec 9 (2020) 181-188 ; <u>https://doi.org/10.18576/ijtfst/090308</u>

[44] S. Shannigrahi, F. Tay, K. Yao, R. Choudhary, Journal of the European Ceramic Society 24

(2004) 163-170 ; https://doi.org/10.1016/S0955-2219(03)00316-9

[45] A. Pinheiro, F. Pereira, M. Santos, H. Rocha, A. Sombra, Journal of materials science 42 (2007) 2112-2120 ; <u>https://doi.org/10.1007/s10853-006-1190-5</u>

[46] W. Liu, X. Wang, D. Tian, C. Xiao, Z. Wei, S. Chen, Materials Sciences and Applications 1 (2010) 91 ; <u>https://doi.org/10.4236/msa.2010.12016</u>

[47] A.R. Molla, A. Tarafder, B. Karmakar, Journal of Alloys and Compounds 680 (2016) 237-246 ; https://doi.org/10.1016/j.jallcom.2016.04.136

[48] E.d.C. Severo, E.R. Abaide, C.G. Anchieta, V.S. Foletto, C.T. Weber, T.B. Garlet, G.C. Collazzo, M.A. Mazutti, A. Gündel, R.C. Kuhn, Materials Research 19 (2016) 781-785 ; https://doi.org/10.1590/1980-5373-MR-2015-0100

[49] Z. Amouzegar, R. Naghizadeh, H. Rezaie, M. Ghahari, M. Aminzare, Ceramics International 41 (2015) 1743-1747 ; <u>https://doi.org/10.1016/j.ceramint.2014.09.119</u>

[50] M.R. Tamtam, R. Koutavarapu, J. Shim, Environmental Research 227 (2023) 115735 ; https://doi.org/10.1016/j.envres.2023.115735

[51] Q. Ning, C. Zhou, Y. Shi, Journal of Solid State Chemistry 290 (2020) 121458 ; https://doi.org/10.1016/j.jssc.2020.121458

[52] W. Zhou, R. Apkarian, Z.L. Wang, D. Joy, Scanning Microscopy for Nanotechnology: Techniques and Applications (2007) 1-40 ; <u>https://doi.org/10.1007/978-0-387-39620-0\_1</u>

[53] Q. Zhou, L. Zhang, L. Zhang, B. Jiang, Y. Sun, Journal of Hazardous Materials 438 (2022) 129438 ; <u>https://doi.org/10.1016/j.jhazmat.2022.129438</u>

[54] T.P. Wendari, M. Ikhram, Ceramics International 48 (2022) 30598-30605 ; https://doi.org/10.1016/j.ceramint.2022.07.003

[55] J. Wang, Y. Shi, H. Sun, W. Shi, F. Guo, Journal of Alloys and Compounds 930 (2023) 167450 ; <u>https://doi.org/10.1016/j.jallcom.2022.167450</u>

[56] M. Shetty, M. Muniyappa, M.N. Rani, V. Gangaraju, P. D. Shivaramu, D. Rangappa, Nanostructured Materials for Environmental Applications (2021) 137-165 ; https://doi.org/10.1007/978-3-030-72076-6 6

[57] G. Fang, J. Liu, X. Yan, D. Wang, J. Israr, T. Xue, Advanced Materials Interfaces 5 (2018) 1800844 ; <u>https://doi.org/10.1002/admi.201800844</u>

[58] K. L. Mary, J. V. Manonmoni, A. M. R. Balan, P. S. Karthik, S. P. Malliappan, Digest Journal of Nanomaterials and Biostructures, 17 (2022) 634-648, https://doi.org/10.15251/DJNB.2022.172.634

[59] X. Wang, L. Zhang, H. Lin, Q. Nong, Y. Wu, T. Wu, Y. He, Rsc Advances 4 (2014) 40029-40035 ; <u>https://doi.org/10.1039/C4RA06035K</u>

[60] B. Ohtani, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 11 (2010) 157-178 ; <u>https://doi.org/10.1016/j.jphotochemrev.2011.02.001</u>

[61] M. Duan, D. Wu, J. Wu, H. Tong, Journal of Materials Science: Materials in Electronics 33 (2022) 7543-7558 ; <u>https://doi.org/10.1007/s10854-022-07898-3</u>

[62] Y. L. Zhuang, X. H. Zhang, L. M. Dong, Y. Li, D. Li, J. H. Dong, Z. W. Liu, S. Tian, L. M. Wang, Y. Dai, Digest Journal of Nanomaterials and Biostructures, 17 (2022) 685-693, https://doi.org/10.15251/DJNB.2022.172.658