Journal of Optoelectronic and Biomedical Materials Vol. 17, No. 3, July – September 2025, p. 187 - 193

Photo-catalysis activity of TiO_2, Co_3O_4, Co_3O_4 @TiO_2, and TiO_2@Co_3O_4 nanoparticles prepared by pulsed-laser ablation

Z. A. Jasim *, J. A. Abd
University of Babylon, College of Science for Women, Department of Laser Physics, Hilla-Najaf Street, Babylon, 51002, Iraq

Water pollution is practically one of the most challenging subjects. Photo-catalysis using nanoparticles is one of the effective techniques that are employed for organic material removal. In this work we explore the optical characteristics and the photo-catalytic activity of Co_3O_4, TiO2, Co_3O_4@TiO_2, and TiO_2@Co_3O_4 nanoparticles prepared by pulsed laser ablation. Effective dye removal has been obtained by using these nanoparticles. Although the prepared nanoparticles exhibit different optical properties, they show close photo-catalytic activities. As single material, the dye removal activity of Co_3O_4 and TiO_2 is nearly terminated after a while. However, by forming core@shell structures of these nanoparticles an effective and continuous dye removal process has been obtained.

(Received July 8, 2025; Accepted August 21, 2025)

Keywords: Co_3O_4, TiO_2, Core-shell, Pulsed-laser ablation, Dye removal

1. Introduction

Nanomaterials greatly advance energy conversion and storage technologies due to their special characteristics such as the large surface area, effective mass [1], and heat and charge transport efficiency [2, 3]. In addition, semiconductor nanostructures have special benefits over their bulk or molecule counterparts due to their distinct characteristics and uses. Narrow emission spectra, continuous absorption bands, excellent chemical stability, processing ease, and adaptability in changing surface functions are some of these characteristics [4].

Research in nanoscience technology is essential to explore the opportunities and the possible applications in addressing environmental problems. There is also a need to develop new approaches that provide advanced capabilities to prevent or effectively deal with highly toxic or difficult-to-degrade pollutants and helping to monitor these pollutants or their effects in more accurate ways. Core-shell nanoparticles represent a type of nanostructure composed of two different materials: an inner core and an outer shell. These particles are mono-dispersed and modifiable, giving them advantages over conventional catalysts particularly in reducing agglomeration. Their size and structure can also be controlled by adjusting their surface properties [5,6].

The medium band gap, broad availability, chemical stability, and nob-toxicity made Titanium dioxide (TiO2) as is one of the most often used materials for photo-catalysis [7]. In addition, researchers have concentrated on producing cobalt oxide (Co_3O_4) nanoparticles (NPs) due to its wide range of uses [8-9]. Co_3O_4 is a p- type semiconductor distinguished by its strong mechanical strength and high chemical stability even at elevated temperatures. In its bulk state, its direct band gap is (1.48 -2.19 eV) [10]. At room temperature, Co_3O_4 is categorized as a paramagnetic semiconductor. However, below 40 K, weak interactions between nearby Co_3O_4 ions cause it to change into an antiferromagnetic behavior [10-11]. Furthermore, Co_3O_4 nanoparticles have good electrical conductivity because of the presence of the Co^{3+} ions [11].

A number of studies have been carried out to investigate the functionality of TiO2 and Co3O4 nanoparticles in photo-catalysis applications. For example, Saleh M. Alluqmani et al [12] explored the effect of synthesis method on the effectiveness of TiO2 nanoparticles at degrading of Methylene blue dye. They used three distinct techniques to prepare the TiO2 nanoparticles: high-

* Corresponding author: scw147.zainab.asid@student.uobabylon.edu.iq
https://doi.org/10.15251/JOBM.2025.173.187

energy ball milling, ultra-sonication, and pulsed laser ablation. A.B. Vennela et al [13] studied the potential of using Co3O4 nanoparticles prepared by sol-gel method in removing methylene blue dye. They achieved 93.8% removal of the dye under optical light irradiation.

In this work we studied the photo-catalytic activity of Co_3O_4, TiO_2, Co_3O_4@TiO_2, and TiO_2@Co_3O_4 nanoparticles prepared by pulsed laser ablation. We explored the effect of the presence of these particles on the degradation rates of methylene blue dye. In addition, we studied the effect of forming core@shell structures on the catalytic activity of these materials.

2. Experimental

The pulsed laser ablation approach was used to create Co3O4, TiO2, Co_3O_4@TiO_2, and TiO_2@Co_3O_4 NPs in water at room temperature. The experimental setup for laser ablation is depicted in Figure (1). The preparation method involved using an Nd-YAG laser with a wavelength of 1064 nm, a repetition rate of (4 Hz), and a pulse energy of (300 mJ).

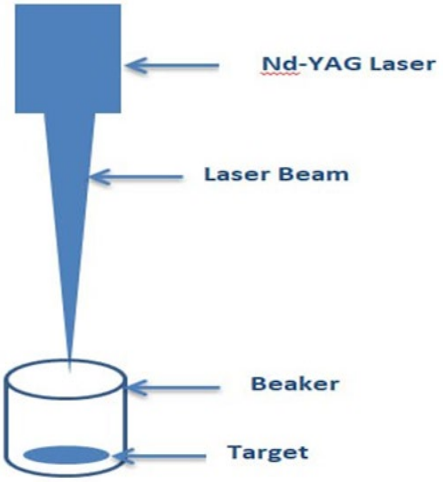

Fig. 1. Experimental setup for the preparation of nanoparticles using laser ablation in liquid (PLAL) technique.

Different numbers of laser pulses were used to prepare Co_3O_4 and TiO2 NPs at different concentrations. 500, 750, and 1000 pulses were used to prepare Co_3O_4, while 100, 200, and 300 laser pulses were used to prepare TiO_2 NPs. The (Co_3O_4@TiO_2) core @shell sample was prepared by using (500) pulses for (Co_3O_4) and (200) pulses for (TiO_2). For the (TiO_2@Co_3O_4) sample 300 pulses were used for (TiO_2) and (500) pulses for (Co_3O_4).

The photo-degradation of the methylene blue (MB) dye was investigated by using different quantities of the produced materials. The removal of the MB dye, i.e. the activity of the nanoparticles, was assessed by monitoring the reduction in the linear optical absorbance of the dye. ACECIL CE2700 UV/Vis spectrophotometer was used to measure the absorbance of the samples. In all tests, 0.01 mM concentration of the dye was used.

3. Results and the discussion

3.1. The optical properties

The absorption spectra of cobalt oxide (Co_3O_4) nanoparticles generated with different numbers of laser pulses and a constant energy (300 mJ) are displayed in Figure (2).

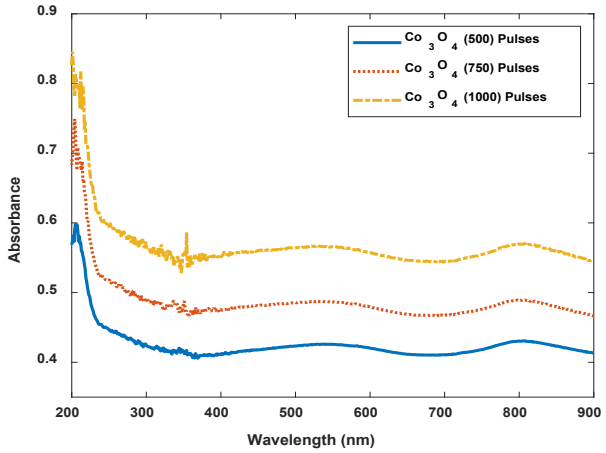

Fig. 2. The absorption spectra of CO_3O_4 NPs prepared with different numbers of lasers pulses.

The absorption spectra of Co_3O_4 in the spectral range of (200 – 900 nm) show two broad absorption bands. The first band has its maximum at about 550 nm and extends approximately from 400 to 650 nm. The second band extends from 730 to 860 nm and peaks at 800 nm. The $O^{-2} \rightarrow Co^{+3}$ and $O^{-2} \rightarrow Co^{+3}$ charge transfers are responsible for these bands [14 -15].

Figure (3) shows the absorption spectra of (TiO_2) NPs.

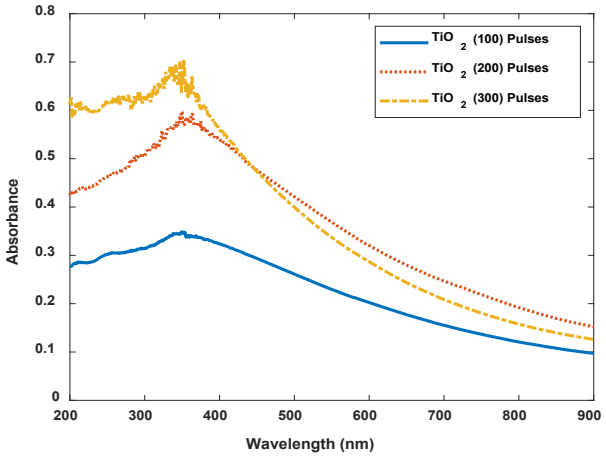

Fig. 3. The absorption spectra of TiO_2 NPs prepared with different numbers of lasers pulses.

The absorption spectra in Figure (3) have maxima at the end of the UV region (at about 360 nm) and decrease gradually at longer wavelengths. O 2p atoms make up the valence band in TiO_2, whereas Ti 3d states make up the conduction band [16]. The electron transitions from O 2p to Ti 3d are the cause of the strong absorption band [17 -18]. The more pulses used the higher the concentration of the nanomaterial the higher the entire absorption curve of the TiO_2 nanoparticles.

Figure (4) shows the absorption spectra of core-shell Co_3O_4@TiO_2 and TiO_2 @Co_3O_4 nanoparticles.

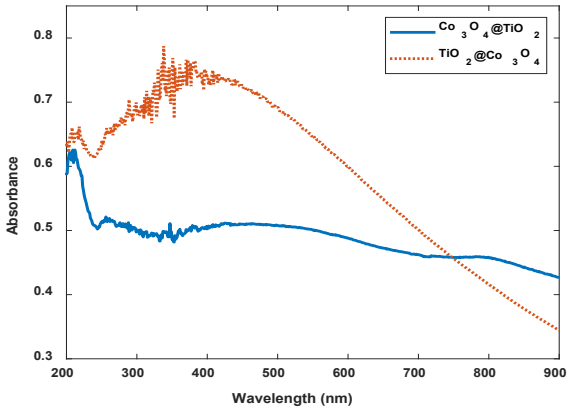

Fig. 4. The absorption spectra of Co_3O_4@Tio_2 NPS and Tio_2@Co_3O_4 NPs.

It can be observed that, the general pattern of the absorption band of Co3O4@TiO2 is more or less similar to the absorption spectrum of Co_3O_4, shown in Figure (2). However, due to the presence of TiO_2 shell, the absorbance of Co_3O_4@TiO_2 is higher in the UV range in comparison with the absorbance the Co_3O_4 NPs.

In the case of TiO_2@Co_3O_4, it can be seen that the absorption spectrum is similar to that of the TiO_2 NPs shown in Figure (3). However, the absorption spectrum of the TiO_2@Co_3O_4 NPs is shifted toward longer wavelengths in comparison to the absorption spectra of the TiO_2 spectrum.

3.2. Photo-catalysis of (Co_3O_4, TiO_2, Co_3O_4 @TiO_2, and TiO_2@Co_3O_4) nanoparticles

The photo-catalysis activity of the prepared nanoparticles was studied via decomposing methylene blue dye in aqueous medium as a pollutant under the assistance of simulated sunlight radiation. Figure (5) shows examples of the absorption spectra of the dye solution containing the prepared nanoparticles at different times.

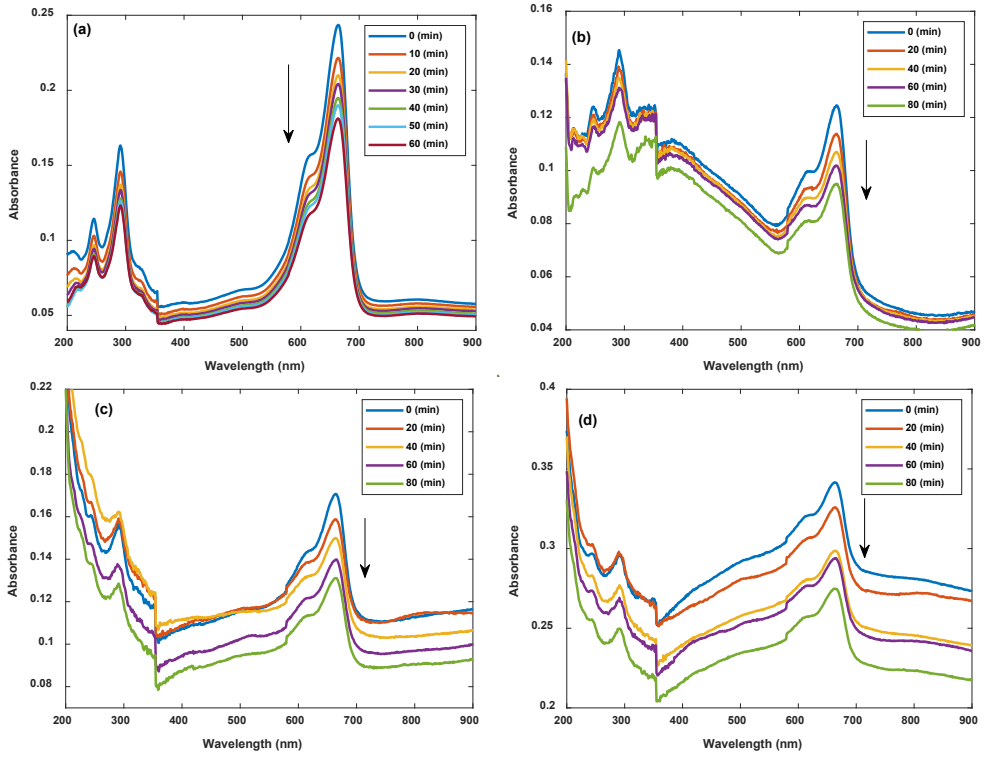

Fig. 5. UV-Vis absorption spectrum of MB dye solution containing (a) Co_3O_4, (b) TiO_2, (c) Co_3O_4 @TiO_2, and (d) TiO_2 @Co_3O_4 nanoparticles at different times under the irradiation of simulated sun light.

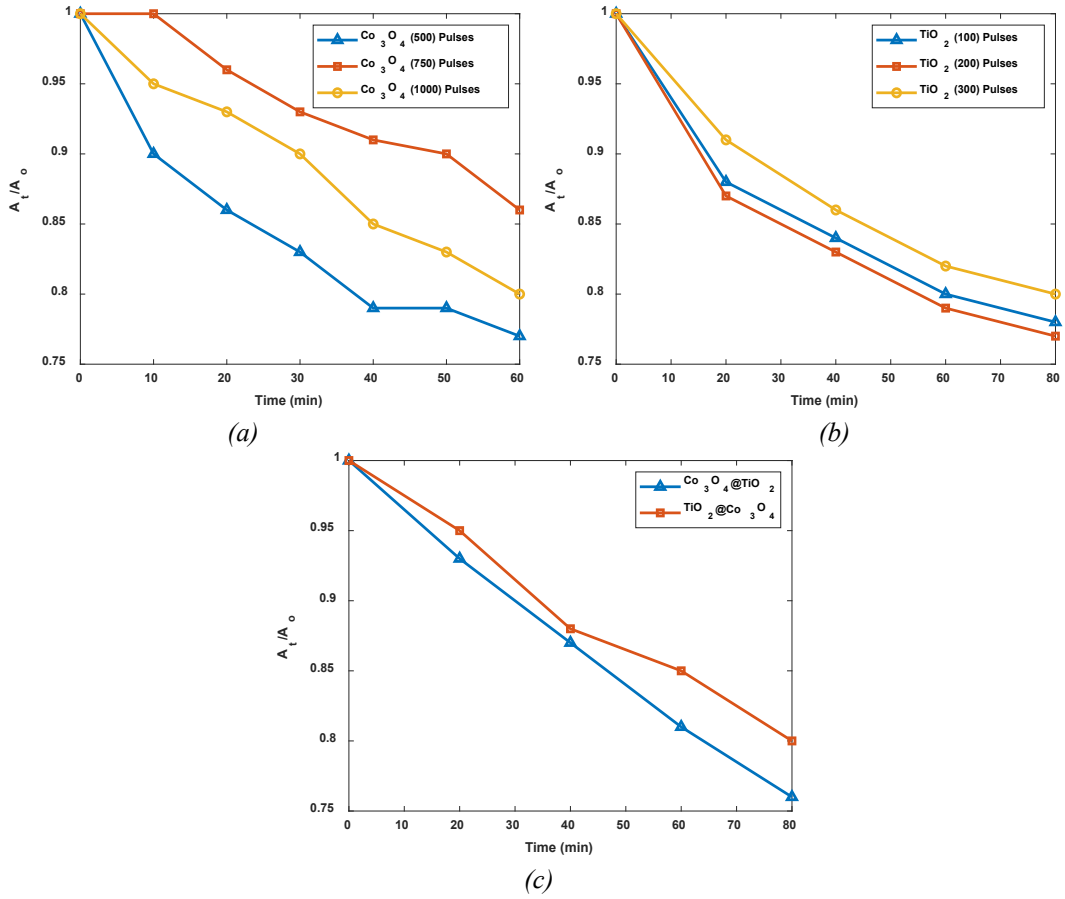

Fig. 6. Photo-degradation of methylene blue dye under visible light using (a) Co_3O_4, (b) TiO_2, and (c) Co_3O_4 @TiO_2 and TiO_2@Co_3O_4 nanoparticles as photo-catalyst.

It can be seen form Figure (6a) that, when (Co_3O_4) nanoparticles are present, the MB dye breaks down gradually. This degradation can be explained by exploring the photo-induced electronic transitions of the NPs. Upon visible light irradiation, photons are absorbed by Co_3O_4 resulting in electrons transitions from the valence band to the conduction band creating electron-hole pairs. The O_2 and H_2O molecules that are adsorbed on the photo-catalyst surface interact with these holes. While the hole combines with water adsorbed on the surface to from hydroxyl radicals ($OH^{\bullet}$), the resultant electron reduces an oxygen molecule to create a superoxide radical ion ($^{\bullet}O_2^-$). The MB dye can be attacked by these active radicals, which can then break it down into simpler compounds [19-20].

The rate of dye deterioration depends on the concentration and the characteristics of the used Co_3O_4 NPs. It can be seen that the highest degradation rate of the dye was obtained by using the Co3O4 NPs prepared with 500 lasers pulses. As this sample contains the lowest NPs concentration, the result is surprising. This can be explained as that the Co3O4 NPs prepared with the lowest pulses number have small average sizes hence a maximum surface to volume ratio. A larger surface area provides larger effective interaction environment for the dye molecules resulting in a higher degradation rate. As the number of laser pulses used increases, the concentration of the produced NPs increases. Although higher particles concentration provides more interactive centers, it leads to the formation of particles of larger sizes via particles aggregation. This reduces the surface to volume ratio. Therefore, the interplay of the opposite effects of concentration and surface to volume ratio determines the degradation rate of the dye. This can be concluded by comparing the degradations rates of Co_3O_4 NPs prepared with 750 and 1000 pulses shown in Figure (6a).

The case is the same when using TiO_2 NPs as photo-catalyst, as shown in Figure (6b). The combination of the number of the NPs and the surface area results in dye degradation ratios that do not have a monotonic increase with the concentration of the NPs.

The photo-induced electrons and holes production is also the mechanism by which the MB dye breakdown in the present of the TiO_2 nanoparticles [21, 22]. MB transforms into oxidized form known as methylene blue Leuco (LMB) during the reduction process [23].

Furthermore, it can be seen from Figures (6 a and b) that the degradation rate of the dye decreases gradually with time and reaches a kind of steady state region beyond 80 minutes. In other words, the interaction between the dye molecules and the NPs stops after a while. However, when using the core@shell structures of these NPs the dye degradation continues monotonically, as shown in Figure (6c). This means that, the formation of Co_3O_4@TiO_2 and/ or TiO_2@Co_3O_4 structures can result in a more effective dye removal. This advantage can be due to charge redistribution or new energy states creation resulting from the combination of Co_3O_4 and TiO_2 materials.

4. Conclusion

In this study, Co_3O_4, TiO_2, Co_3O_4@TiO_2, and TiO_2@Co_3O_4 nanoparticles (NPs) were prepared by pulsed laser ablation in liquids and used as photo-catalysts for methylene blue dye. These NPs show effective photo-catalytic activity under the irradiation of simulated sunlight radiation. The degradation rate of the dye depends on the interplay of the effects of the number of NPs and the total surface to volume ratio of these particles. In addition, when using NPs of single material, the dye degradation reaches is terminated after a while. However, the core@shell structures of the Co_3O_4 and TiO_2 material can provide continuous photo-catalysis process resulting in more effective dye removal.

References

[1] Y. Yan, G. Chen, P. She, G. Zhong, W. Yan, B.Y. Guan, Y. Yamauchi, Advanced Materials, 32 (44), 200465 (2020); https://doi.org/10.1002/adma.202004654
[2] Y. Wang, P. Yang, L. Zheng, X. Shi, H. Zheng, Energy Storage Mater. 26 (2020) 349; https://doi.org/10.1016/j.ensm.2019.11.006.
[3] K. Qu, Y. Wang, A. Vasileff, Y. Jiao, H. Chen, Y. Zheng, Journal of Materials Chemistry. A 6 (44), 21827 (2018); https://doi.org/10.1039/C8TA05245J
[4] G. Chen, J. Seo, C. Yang, P.N. Prasad, Chemical Society Reviews. 42 (21), 8304 (2013); https://doi.org/10.1039/C3CS60054H.
[5] Y-C. Liang, N-C. Xu, C.C. Wang, Da –Hua Wei, Materials 10(7), 778 (2017); https://doi.org/10.3390/ma10070778
[6] Y-C. Liang, C-C. Chung, Ya–Ju Lo, Materials,9(12),2014(2016); https://doi.org/10.3390/ma9121014
[7] A. H. Navidpour, S. Abbasi, D. Li, A. Mojiri, J. Zhou, Catalysts, 13(2), 232(2023); https://doi.org/10.3390/catal13020232.
[8] K. Agilandeswari, A. Ruban Kumar, International Journal of Chem Tech Research 6(3), 2089 (2014)
[9] S. Shadrokh, M. Farahmandjou, T.P. Firozabadi, Physical Chemistry Research 4 (2), 153 (2016); https://www.researchgate.net/publication/318887305.
[10] S. Aisida ,K. Ugwu, P. Akpa, A. Nwanya, P. Ejikeme, S. Botha, I. Ahmad, M .Maaza, F. Ezema, Materials Chemistry and Physics 237 (1),121859 (2019); https://doi.org/10.1016/j.matchemphys.2019.121859.
[11] N. Madubuonu, S. Aisida, A. Ali, I. Ahmad, T. Zhao, S. Botha, M. Maaza, F. Ezema, Journal of Photochemistry and Photobiology B: Biology 199, 111601(2019); https://doi.org/10.1016/j.jphotobiol.2019.111601

[12] S. Alluqmani, A. AL-Zahrani, H. Almarri, N. Alabdallah, Polish Journal of Environmental Studie 33 (2) ,1495 (2025); https://doi.org/10.15244/pjoes/184150
[13] A. B. Vennela, D. Mangalaraj, N. Muthukumarasamy, S. Agilan, K.V. Hemalatha 14(4), 3535 (2019), International Journal of Electrochemical Science; https://doi.org/10.20964/2019.04.40
[14] S. Farhadi, J. Safabakhsh, P. Zaringhadam, Journal of Nanostructure in Chemistry 3(69) (2013); https://doi.org/10.1186/2193-8865-3-69
[15] A. B. Vennela, D. Mangalaraj, N. Muthukumarasamy, S. Agilan, K. V. Hemalatha, International Journal of Electrochemical Science 14 (4), 3535(2019); https://doi.org/10.20964/2019.04.40
[16] Y. Nagao, A. Yoshikawa, K. Koumoto, T. Kato, Y. Ikuhara, H. Ohta, Applied Physics Letters 97, 172112 (2010); https://doi.org/10.1063/1.3507898
[17] J. Saimon, S. Madhat, K. Khashan, A. Hassan, International Journal of Modern Physics B, 32, 1850341 (2018); https://doi.org/10.1142/S0217979218503411
[18] A. S. Nikolov, P. A. Atanasov, D. R. Milev, T. R. Stoyanchov, A. D. Deleva, Z. Y. Peshev, 255 (1), 5351 (2009); https://doi.org/10.1016/j.apsusc.2008.09.007
[19] H. Li, G. Tao Fei, M. Fang, P. Cui, X. Guo, P. Yana, Li De Zhang, Applied Surface Science 257, 6527 (2011); https://doi.org/10.1016/j.apsusc.2011.02.066
[20] N. Qutub, B. M. Pirzada, K. Umar, S. Sabir, Journal of Environmental Chemical Engineering 4, 808 (2016); https://doi.org/10.1016/j.jece.2015.10.031
[21] V. K Palanisamy, K. Manoharan, K. Raman, R. Sundaram, Journal of Materials Science: Materials in Electronics 31, 14795 (2020); https://doi.org/10.1007/s10854-020-04043-w
[22] H. Saufi, M. El Alouani, S. Alehyen, M. El Achouri, J. Aride, M. Taibi, International Journal of Chemical Engineering 2020, 9498349 (2020); https://doi.org/10.1155/2020/9498349
[23] S. Naraginti, Yi Li, Journal of Photochemistry and Photobiology B: Biology 170 ,225 (2017); https://doi.org/10.1016/j.jphotobiol.2017.03.023