

RESEARCH

Optimizing Titanium-dioxide Photocatalysts for Efficient Degradation of Methylene Blue: The Influence of Hydrothermal Reaction Time

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ABSTRACT

This research explores the influence of hydrothermal reaction time on the structural, optical and morphological properties of TiO₂ nanoparticles. The photocatalytic performance of TiO₂ nanoparticles for the degradation of Methylene Blue is also evaluated and a co-relation between reaction time and photocatalytic efficiency is established. Structural analysis reveals well-defined anatase phases with enhanced crystallinity at extended reaction times. UV-Visible spectroscopy demonstrates a red shift in absorption with increased reaction time, indicative of tunable optical properties. FE-SEM images show an increase in particle agglomeration with increasing hydrothermal duration. Photocatalytic experiments underline TiO₂-12 as the most efficient catalyst, achieving a remarkable 97% degradation within 105 minutes. The Langmuir-Hinshelwood kinetics model elucidates the reaction rate dependence on hydrothermal reaction time, emphasizing the role of synthesis parameters on the photocatalytic activity of TiO₂. Moreover, TiO₂-12 sample shows an enhanced degradation rate compared to other samples. Based on the findings, a possible mechanism of photocatalytic degradation of Methylene Blue is proposed.

KEYWORDS

Titanium-dioxide, Photocatalysis, Hydrothermal synthesis, Methylene Blue.

INTRODUCTION

The extensive use of synthetic dyes such as Methylene Blue, Malachite Green, Acid Red etc. in various industrial applications, has raised many concerns due to its environmental effects [1]. When released into aquatic ecosystems, either through industrial discharge or improper disposal, these dyes can exert detrimental impacts on aquatic life [2]. Studies have indicated that exposure to Methylene Blue (MB) leads to toxicity in aquatic organisms, affecting fish, algae, and other aquatic fauna [2,3]. Furthermore, Methylene Blue has also been associated with human health effects including skin and eye irritation [4], respiratory irritation upon inhalation [5], and concerns regarding potential carcinogenicity [6]. The potential toxicity of such dyes emphasises the need for responsible use, disposal, and treatment methods to reduce

their negative effects on aquatic ecosystems and human health [7,8]. In addressing the treatment of dye-contaminated wastewater, an array of methodologies are employed, encompassing biological methods such as activated sludge systems and bioremediation [9,10], physical strategies including adsorption and filtration [11,12], chemical methodologies such as coagulation-flocculation and precipitation [13,14], membrane-based technologies such as ultrafiltration and reverse osmosis [15,16], electrochemical techniques including electrocoagulation and electro-oxidation [17,18], and advanced oxidation processes (AOPs) typified by ozonation and photocatalysis [19,20].

Among the aforementioned technologies, photocatalysis is rapidly advancing within the domains of materials science and chemistry [21]. Fundamentally, photocatalysis involves the use of semiconductor materials

to harness and convert light energy into chemical reactions [22–24]. This process has enormous potential for a variety of applications, including environmental remediation, water purification, and renewable energy production [25] [26]. Common semiconductors preferred by the researchers for the photocatalytic process include ZnS [27,28], CdS [29,30], WO₃ [31,32], Cu₂O [33,34], ZnO [35–37], Al₂O₃ [38,39], TiO₂ [40,41], BiVO₄ [42,43], g-C₃N₄ [44,45] etc.

In particular, TiO₂ is being extensively studied by the researcher owing to its outstanding stability, wide bandgap, high photocatalytic activity, and additional advantages such as low cost, abundance and biocompatibility [46–49]. TiO₂ can be synthesized via different techniques including but not limited to, sol-gel [50,51], Hydrothermal/Solvothermal [52,53], Chemical Precipitation [54], Spray Pyrolysis [55] and Chemical Vapour Deposition [56].

However, high temperature, pressure hydrothermal synthesis has many advantages such as high crystallinity of the products [57], uniform particles sizes [58], high specific surface areas [59], low cost and energy consumption etc [60]. Controlling the hydrothermal reaction conditions allows for tailoring the structural and morphological properties of TiO₂ for photocatalytic applications. Kontos A. *et. al.* proposed that the hydrothermal treatment of commercial P25 powder for different time durations (1 to 10 days), brought modifications to surface areas and particles sizes enhances photocatalytic efficiency of TiO₂ up to two times for the duration changed from 1 day to 4 days [61]. Testino A. *et. al.* established a correlation between particle sizes and photocatalytic activity of TiO₂ in phenol degradation. Precise control over phase structure and morphology was achieved by adjusting the pH, temperature and duration of hydrothermal reaction [62]. In another study, Lu C. *et. al.* demonstrated that the morphology of TiO₂ nanoparticles changed from rod-like to polyhedral shape when hydrothermal duration was increased. This change in shape resulted in lower surface area and in turn reduced the photocatalytic activity [63]. The study by Tao J. *et. al.* confirmed a change in morphology TiO₂ nanoarrays from nanorods to nanoflowers with an increase in hydrothermal reaction time. The nanoflowers showed better efficiency in Methyl

Orange degradation which was attributed to their higher surface areas [64]. Building upon the existing literature, we attempt to test the effects of hydrothermal conditions on the photocatalytic activity of TiO₂.

In this study, TiO₂ photocatalysts are synthesized at various hydrothermal reaction times at a fixed temperature of 180°C. Structural and morphological properties of the TiO₂ samples are examined by XRD, UV-Vis spectroscopy, FTIR and FE-SEM. Photocatalytic degradation of Methylene Blue is carried out to study the effect of reaction time on the photocatalytic efficiency of TiO₂ samples. Mechanism of photocatalytic degradation of Methylene Blue is also proposed.

EXPERIMENTAL

Chemicals and Reagents

Titanium tetra-isopropoxide (TTIP) (>98% pure, Sigma Aldrich), Hydrochloric Acid (35-38%, Thomas Baker), Ethanol and DI water were used for TiO₂ synthesis. Methylene Blue (Loba Chemie) was used as a model pollutant for photodegradation experiments. All the reagents were used as received without any further purifications.

Synthesis of TiO₂ Nanoparticles

The schematic illustration of the synthesis procedure is shown in **Fig. 1**. Solution ‘A’ was prepared by mixing 4 mL of titanium tetra-isopropoxide (TTIP) with 20 mL of ethanol under magnetic stirring for 1 hour. Solution ‘B’ containing 4 mL of 0.8 M hydrochloric acid in 10 mL ethanol was added dropwise to solution ‘A’. The reaction mixture was then stirred continuously for another hour before being transferred to a Teflon-coated stainless-steel autoclave and subjected to reaction conditions at 180°C for 12, 18 and 24 hours. Post reaction, the samples were filtered and dried overnight at 100°C. Lastly, the samples were annealed at 350°C for 2 hours in a muffle furnace to obtain TiO₂ powders. The samples were labelled TiO₂-12, TiO₂-18 and TiO₂-24, corresponding to the reaction time of synthesis.

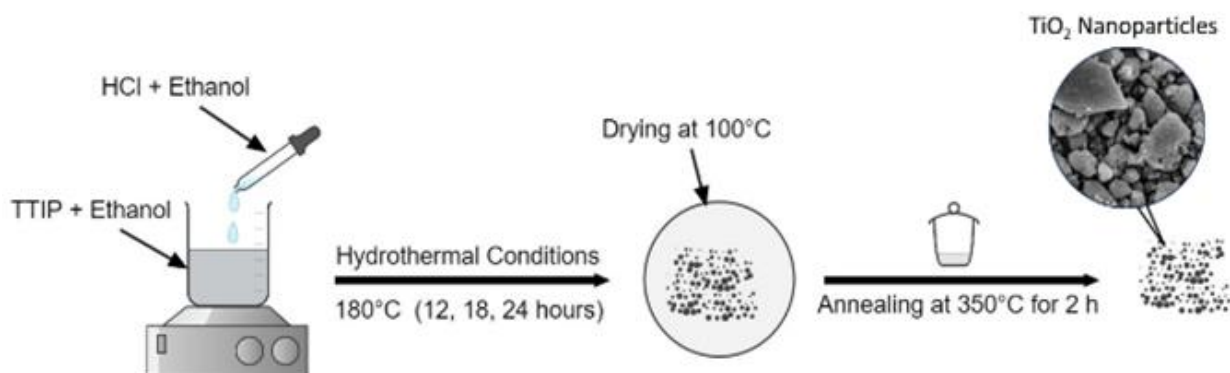


Fig. 1. Schematic diagram of Synthesis of TiO₂ nanoparticles.

Characterization Techniques

Samples were scanned by X-ray diffractometer (Rigaku MiniFlex 600, Japan) to study their structural properties. Surface morphologies of the photocatalysts were analyzed by Scanning electron microscopy (FEI Nova NanoSEM 450). In addition, the light absorption spectra and band gap were obtained via UV-Visible spectroscopy (Shimadzu, Model UV-2600, Kyoto, Japan).

Photocatalytic experiments

100 mL of aqueous Methylene Blue solution of 10 ppm concentration was taken in a glass beaker. An appropriate amount of the TiO₂ photocatalyst was dropped into this solution. The concentration of the photocatalyst in the dye solution was maintained at 1 g/L. To attain adsorption-desorption equilibrium, the reaction mixture was stirred under dark conditions inside the reactor chamber for 30 minutes. Photocatalytic degradation of Methylene Blue was carried out under radiation from two UV sources; UV-A (Philips, F18W/T8, λ_{max}=365 nm) and UV-C (Philips, F18/T8, λ_{max}=295 nm) positioned at a fixed distance from the beaker for consistent illumination.

To ensure continuous catalyst-dye molecule contact, the reaction mixture was stirred throughout the experiment. About 3 mL of the dye solution was taken out every 15 minutes and analyzed using UV-vis spectra (Perkin Elmer Lambda 265, USA) to measure the residual dye concentration. The percentage dye degradation and photocatalytic efficiency of the photocatalyst with respect to irradiation time were assessed by monitoring the reduction in absorbance at 664 nm wavelength, which corresponds to Methylene Blue's absorption peak. A schematic representation of the photocatalytic experiment is shown in Fig. 2.

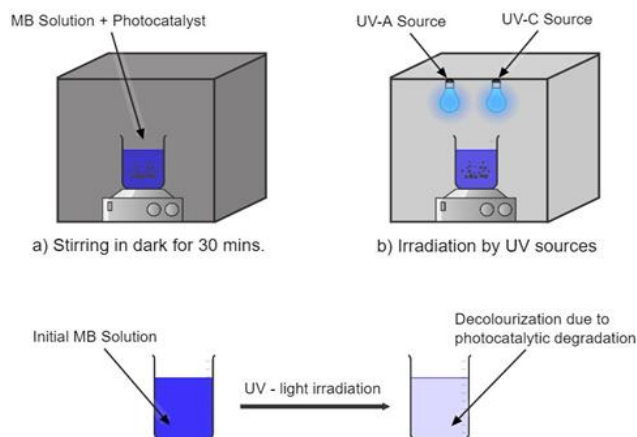


Fig. 2. A schematic representation of the Photocatalytic Experiment.

The photocatalytic degradation efficiency η of was calculated using the following equation [65,66]:

$$\eta = \frac{C_0 - C}{C_0} \times 100$$

where, C_0 is the initial dye concentration and C is the dye concentration at time t .

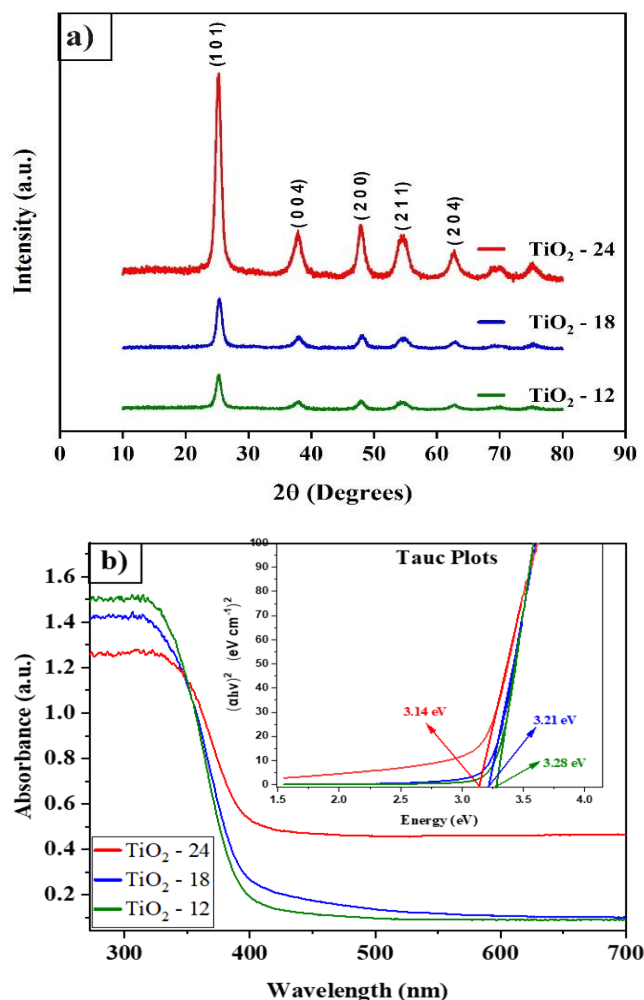


Fig. 3. (a) XRD patterns of TiO₂-12, 18, 24 hours and (b) UV-vis. absorbance curves with Tauc plots in the inset.

RESULTS AND DISCUSSION

X-Ray Diffraction Studies

XRD patterns of the synthesized samples are shown in Fig. 3(a). All of the samples exhibit diffraction peaks that correspond to the pure anatase phase of TiO₂ [67–70]. There are no discernible diffraction peaks indicative of rutile or brookite phases in any of the samples. The diffraction peaks observed at $2\theta = 25.2^\circ, 37.8^\circ, 47.9^\circ$ and 54.9° were indexed to (101), (004), (200), (211) and (204) crystal planes respectively. The intensities of these peaks increased without peak broadening with increase in reaction time indicating an increase in crystallinity. However, no peak broadening suggests no change in crystallite sizes. The average crystallite sizes were calculated using Scherrer's equation [71]:

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl} \cos\theta}$$

The crystallite size for each (h k l) plane is denoted by D_{hkl} . λ represents the wavelength of the X-ray source, in this case 1.5406 Å for the Cu source. Bragg's angle, denoted in radians as θ . The full width at half maxima (FWHM) for the (h k l) plane is denoted by β_{hkl} , which is also measured in radians. The crystallite shape factor, denoted as K, has a universally accepted value of 0.9.

UV-Visible Absorption Spectroscopy

Fig. 3(b) shows the UV-vis DRS spectra of the TiO₂ samples. All the samples have a similar absorption profile which show significant absorption in 350 nm to 400 nm region. This could be attributed to the transition of electrons from valance band to the conduction band due to excitation [72]. It may be noted that with an increase in reaction time, the absorption edges of the samples are shifted towards longer wavelength region (red shift). It is clear from the absorption spectra that TiO₂ can only effectively absorb light with wavelength less than 420 nm, i.e. only in the UV region of the electromagnetic spectrum [73,74].

The band-gap energies of the TiO₂ samples are estimated from the Tauc Plot by plotting $(\alpha h\nu)^2$ against energy of light (h ν) [75]. Where, α is the absorption coefficient, ν is the frequency of light and h is the Plank's constant. The x-intercept of the extrapolated linear region in the Tauc Plot gives the value of the band-gap energy. A quantitative summary of XRD and UV-Vis absorption studies is given in **Table 1**. It can be concluded that the hydrothermal reaction time has a considerable impact on the optical properties of TiO₂. The band gap energy was found to decrease with increasing reaction time.

Table 1. Quantitative summary of XRD and UV-Vis absorption studies.

Sample	Absorption Edge (nm)	Band-gap Energy (eV)	Crystallinity (%)	Average Grain Size (nm)
TiO ₂ - 12	397	3.28	68.29	6.32
TiO ₂ - 18	402	3.21	70.83	6.71
TiO ₂ - 24	412	3.14	83.32	6.75

Scanning Electron Microscopy

The surface morphology of as synthesized TiO₂ is analysed through FE-SEM images shown in **Fig. 4(a-c)**. The samples consist of small spherical particles which have formed larger aggregates. The aggregation of the particles becomes more pronounced as the hydrothermal time duration is increased up to 24 hours. This observed agglomeration of particles can be attributed to prolonged interactions and nucleation processes occurring during the hydrothermal reaction.

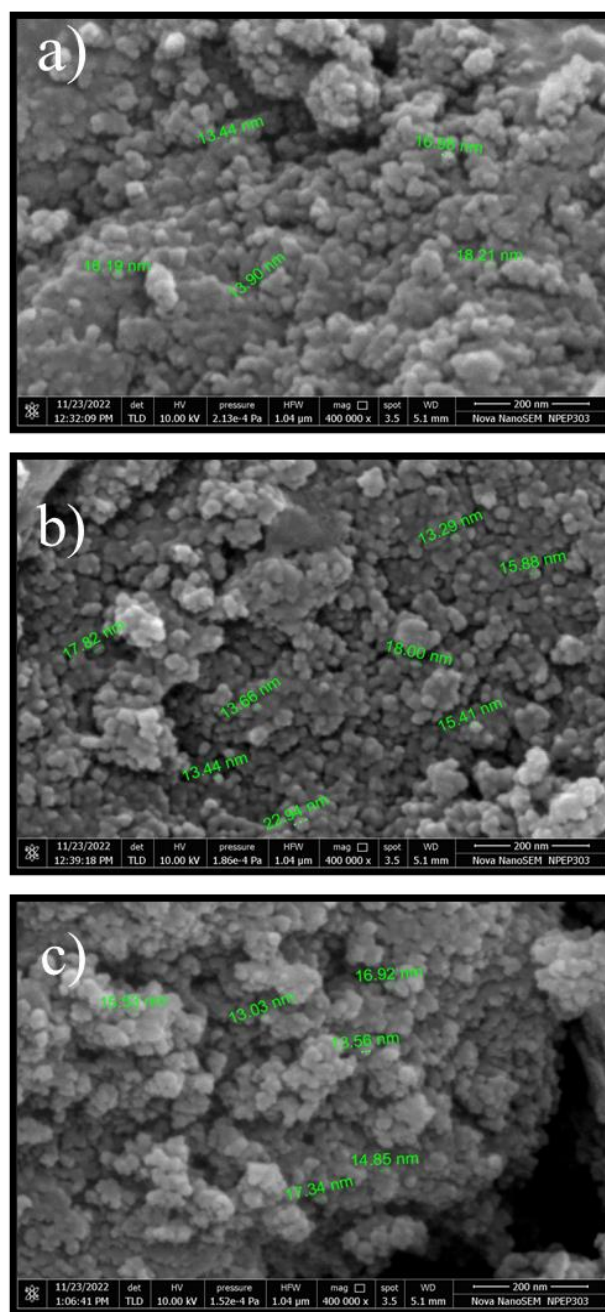


Fig. 4. FE-SEM images of a) TiO₂-12 b) TiO₂-18 and c) TiO₂-24 at scale 200 nm.

Photocatalytic Activity

The effect of hydrothermal reaction time on the photocatalytic activity of TiO₂ samples was explored using Methylene Blue as the target dye. The catalyst concentration was fixed at 1 g/L and the photocatalytic degradation of Methylene Blue was enforced under radiation from UV light sources. **Fig. 5(a)** displays the absorbance spectra of the Methylene Blue solution with respect to irradiation time. Evidently, an observable decline in absorbance values at the reference wavelength of 664 nm

is obvious with increasing irradiation time, indicating the photocatalytic degradation of the Methylene Blue solution. **Fig. 5(b)** illustrates the photocatalytic degradation profiles of Methylene Blue using different catalysts. In the absence of any catalyst, the photodegradation of Methylene Blue exhibited a nominal efficacy, with only a marginal 3% reduction in initial concentration observed over a 105-minute irradiation period. Conversely, when employing TiO₂-12 as a catalyst within the same time frame, a remarkable degradation efficiency of approximately 97% was achieved. This notable disparity underscores the pivotal role of TiO₂ photocatalyst in enhancing the photodegradation kinetics of Methylene Blue under irradiation conditions.

Remarkably, TiO₂-12, TiO₂-18, and TiO₂-24 exhibit degradation efficiencies of 97.8%, 87.5%, and 71.4%, respectively, following a 105-minute irradiation period. This observed trend suggests that prolonged hydrothermal reaction times, leading to increased particle aggregation, may result in reduced availability of active catalytic sites, thereby reducing the photocatalytic efficiencies.

The photocatalytic degradation of dyes follows the Langmuir-Hinshelwood kinetic model [76] where, the degradation rate depends on the amount of dye molecules present in the solution. The kinetic model is represented by the following equation:

$$-r = -\frac{dc}{dt} = \frac{k'KC}{1+KC}$$

where C is concentration of pollutant dye (Methylene Blue) solution, k' is reaction rate constant and K is adsorption equilibrium constant. If concentration of pollutant dye is low the KC << 1 then the reaction can be expressed as,

$$-\frac{dc}{dt} = k'KC$$

$$-\frac{dc}{dt} = kC$$

where $k=k'K$ is the rate constant of pseudo first order reaction. Logarithmic form of the equation is [76]:

$$\ln\left(\frac{C}{C_0}\right) = -kt$$

Thus, the slope of $\ln(C/C_0)$ vs t graph gives the rate constant for the reaction. Linear fits of Langmuir-Hinshelwood reaction kinetics model are represented in **Fig. 5(c)** and the comparison of reaction rate constants for different photocatalysts is visualized in **Fig. 5(d)**. **Table 2** quantitatively summarizes the Methylene Blue degradation process under different catalysts.

Table 2. Quantitative summary of Photocatalytic Degradation of MB after 105 mins of irradiation time.

Sample	Photocatalytic Efficiency (%)	Degradation Rate (min ⁻¹)
TiO ₂ - 12	97.8	0.03218
TiO ₂ - 18	87.5	0.01872
TiO ₂ - 24	71.4	0.00965

From **Table 2**, we can infer that the hydrothermal reaction time affects the rate of dye degradation. TiO₂-12 photocatalyst shows highest degradation rate of 0.0321min⁻¹ which is significantly higher than the degradation rates of TiO₂-18 (0.0187 min⁻¹) and TiO₂-24 (0.0096 min⁻¹).

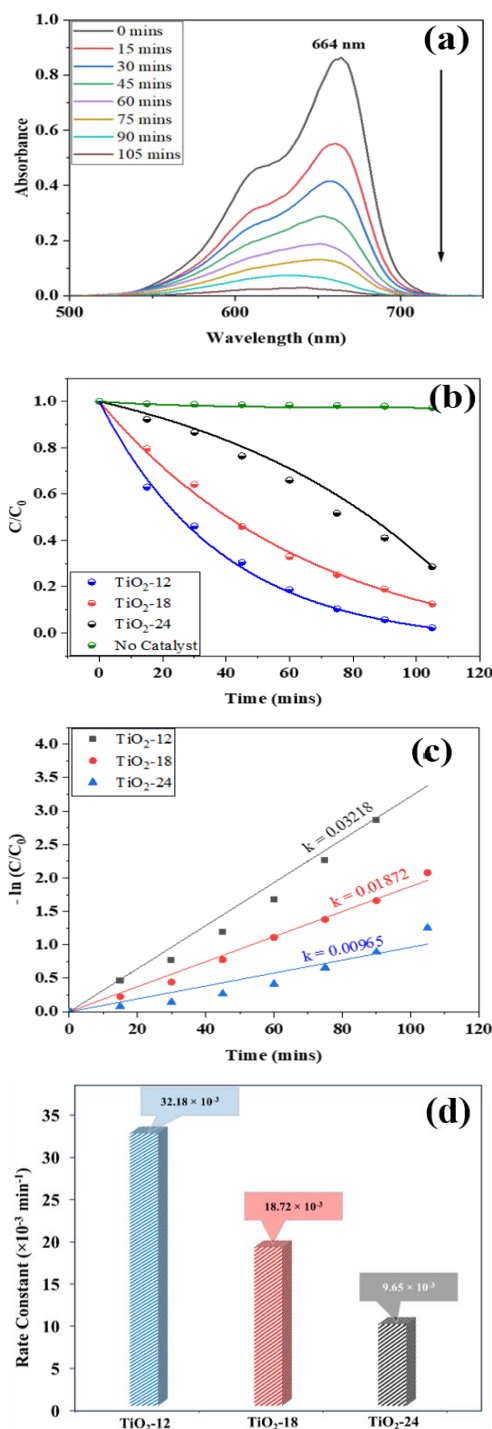


Fig. 5. a) Time dependent absorption spectra of Methylene Blue. b) Degradation profiles of MB under various catalysts. c) First-order reaction kinetics for various catalysts and d) Comparison of reaction rate constants for the different catalysts.

Mechanism of Photodegradation

The intricate process of photocatalytic degradation involves multiple sequential steps. Building upon the theoretical and experimental discussions provided earlier, we propose a plausible mechanism for the photocatalytic degradation of Methylene Blue, as illustrated schematically in Fig. 6.

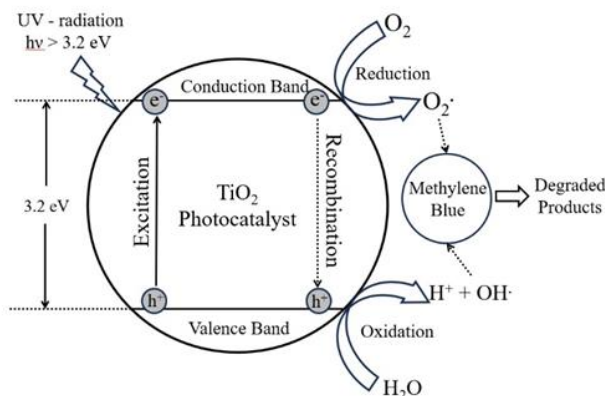
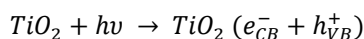
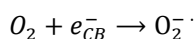
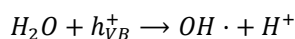


Fig. 6. Schematic representation of the mechanism of photocatalytic degradation of MB by TiO₂ photocatalyst

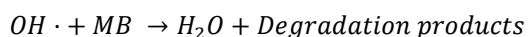
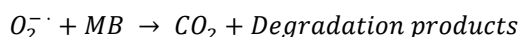
While stirring under dark conditions, Methylene Blue molecules are adsorbed onto the TiO₂ surface. This step is crucial for the subsequent reactions to occur. Under irradiation with light energy equal to or greater than the band gap energy of the TiO₂ catalyst (approximately 3.2 eV), electron excitation induces a transition from the valence band to the conduction band, generating electron-hole pairs:



These photogenerated electron-hole pairs can subsequently engage in reactions with water and oxygen, resulting in the formation of highly reactive species, namely hydroxyl radicals (OH·) and superoxide radicals (O₂⁻):



These generated reactive oxygen species attack and degrade Methylene Blue molecules through reduction and oxidation reactions leading to the breakdown of Methylene Blue into smaller and less harmful by-products. The final products of the photocatalytic degradation process are typically water, carbon di-oxide and other smaller organic compounds.



The mineralization ensures complete degradation of Methylene Blue into non-toxic products [77].

This proposed mechanism provides insights into the photoinduced degradation pathway of Methylene Blue, clarifying the pivotal role of TiO₂ in orchestrating the generation of reactive species and subsequent degradation processes.

CONCLUSION

In summary, this study systematically investigated the impact of hydrothermal reaction time on the synthesis, structural properties, and photocatalytic performance of TiO₂ nanoparticles for Methylene Blue degradation. The XRD analysis revealed that all synthesized samples maintained the pure anatase phase, with enhanced crystallinity observed with prolonged reaction times. UV-Visible spectroscopy demonstrated a red shift in absorption edges with increased reaction time, indicating a tuneable optical response. Photocatalytic experiments demonstrated the efficacy of TiO₂ in Methylene Blue degradation, with TiO₂-12 exhibiting superior performance, achieving a remarkable 97% degradation within a 105-minute irradiation period. The Langmuir-Hinshelwood kinetics model further elucidated the reaction rate dependence on the hydrothermal reaction time, and TiO₂-12 exhibited the highest reaction rate among the investigated samples.

In conclusion, this comprehensive investigation establishes the significance of hydrothermal reaction time in tailoring the structural and photocatalytic properties of TiO₂, addressing dye pollution in environmental applications.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

SUPPORTING INFORMATION

Supporting informations are available online at journal website.

REFERENCES

- Vasiljevic, Z.Z.; Dojcinovic, M.P.; Vujanecvic, J.D.; Jankovic-Castvan, I.; Ognjanovic, M.; Tadic, N.B.; Stojadinovic, S.; Brankovic, G.O.; Nikolic, M. V.; *R Soc Open Sci*, **2020**, *7*.
- Li, S.; Cui, Y.; Wen, M.; Ji, G.; *Toxics*, **2023**, *11*.
- Oladoye, P.O.; Ajiboye, T.O.; Omotola, E.O.; Oyewola, O.J.; *Results in Engineering*, **2022**, *16*, 100678.
- Khan, I.; Saeed, K.; Zekker, I.; Zhang, B.; Hendi, A.H.; Ahmad, A.; Ahmad, S.; Zada, N.; Ahmad, H.; Shah, L.A.; Shah, T.; Khan, I.; *Water* **2022**, Vol. 14, Page 242, **2022**, *14*, 242.
- Oladoye, P.O.; Ajiboye, T.O.; Omotola, E.O.; Oyewola, O.J.; *Results in Engineering*, **2022**, *16*, 100678.
- Abdellah, M.H.; Nosier, S.A.; El-Shazly, A.H.; Mubarak, A.A.; *Alexandria Engineering Journal*, **2018**, *57*, 3727–3735.
- Houas, A.; Lachheb, H.; Ksibi, M.; Elaloui, E.; Guillard, C.; Herrmann, J.M.; *Appl Catal B*, **2001**, *31*, 145–157.

8. Petit, M.; Michez, L.; Raimundo, J.M.; Malinowski, T.; Dumas, P.; *Eur J Phys*, **2016**, 37, 065808.
9. Soliman, M.F.; Rashed, M.N.; Ahmd, A.A.; *Water Air Soil Pollut*, **2023**, 234, 1–13.
10. Upendar, G.; Dutta, S.; Bhattacharya, P.; Dutta, A.; *Water Sci Technol*, **2017**, 75, 1572–1583.
11. Munir, M.; Nazar, M.F.; Zafar, M.N.; Zubair, M.; Ashfaq, M.; Hosseini-Bandegharai, A.; Khan, S.U.D.; Ahmad, A.; *ACS Omega*, **2020**, 5, 16711–16721.
12. He, X.; Male, K.B.; Nesterenko, P.N.; Brabazon, D.; Paull, B.; Luong, J.H.T.; *ACS Appl Mater Interfaces*, **2013**, 5, 8796–8804.
13. Ihaddaden, S.; Aberkane, D.; Boukerroui, A.; Robert, D.; *Journal of Water Process Engineering*, **2022**, 49, 102952.
14. Kazadi Mbamba, C.; Batstone, D.J.; Flores-Alsina, X.; Tait, S.; *Water Res*, **2015**, 68, 342–353.
15. He, Z.; Lyu, Z.; Gu, Q.; Zhang, L.; Wang, J.; *Colloids Surf A Physicochem Eng Asp*, **2019**, 578, 123513.
16. Khanzada, N.K.; Farid, M.U.; Kharraz, J.A.; Choi, J.; Tang, C.Y.; Nghiem, L.D.; Jang, A.; An, A.K.; *J Memb Sci*, **2020**, 598, 117672.
17. Särkkä, H.; Bhatnagar, A.; Sillanpää, M.; *Journal of Electroanalytical Chemistry*, **2015**, 754, 46–56.
18. Moussa, D.T.; El-Naas, M.H.; Nasser, M.; Al-Marri, M.J.; *J Environ Manage*, **2017**, 186, 24–41.
19. Agustina, T.E.; Ang, H.M.; Vareek, V.K.; *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, **2005**, 6, 264–273.
20. Al-Mamun, M.R.; Kader, S.; Islam, M.S.; Khan, M.Z.H.; *J Environ Chem Eng*, **2019**, 7, 103248.
21. Anucha, C.B.; Altin, I.; Bacaksiz, E.; Stathopoulos, V.N.; *Chemical Engineering Journal Advances*, **2022**, 10, 100262.
22. Pathak, D.; Sharma, A.; Sharma, D.P.; Kumar, V.; *Applied Surface Science Advances*, **2023**, 18, 100471.
23. Mersal, M.; Zedan, A.F.; Mohamed, G.G.; Hassan, G.K.; *Scientific Reports* **2023** 13:1, **2023**, 13, 1–15.
24. Begum, S.; Narwade, V.N.; Halge, D.I.; Jejurikar, S.M.; Dadge, J.W.; Muduli, S.; Mahabole, M.P.; Bogle, K.A.; *Mater Res Express*, **2020**, 7, 025013.
25. Hassaan, M.A.; El-Nemr, M.A.; Elkatory, M.R.; Ragab, S.; Niculescu, V.C.; El Nemr, A.; *Topics in Current Chemistry* **2023** 381:6, **2023**, 381, 1–54.
26. Yang, X.; Wang, D.; *ACS Appl Energy Mater*, **2018**, 1, 6657–6693.
27. Meng, Y.; Liu, G.; Zuo, G.; Meng, X.; Wang, T.; Ye, J.; *Nanoscale*, **2022**, 14, 14455–14465.
28. Khodamorady, M.; Bahrami, K.; *Scientific Reports* **2023** 13:1, **2023**, 13, 1–16.
29. Cheng, L.; Xiang, Q.; Liao, Y.; Zhang, H.; *Energy Environ Sci*, **2018**, 11, 1362–1391.
30. Chen, Y.; Zhong, W.; Chen, F.; Wang, P.; Fan, J.; Yu, H.; *J Mater Sci Technol*, **2022**, 121, 19–27.
31. Liu, X.; Zhai, H.; Wang, P.; Zhang, Q.; Wang, Z.; Liu, Y.; Dai, Y.; Huang, B.; Qin, X.; Zhang, X.; *Catal Sci Technol*, **2019**, 9, 652–658.
32. Dong, P.; Hou, G.; Xi, X.; Shao, R.; Dong, F.; *Environ Sci Nano*, **2017**, 4, 539–557.
33. Wu, Y.A.; McNulty, I.; Liu, C.; Lau, K.C.; Liu, Q.; Paulikas, A.P.; Sun, C.J.; Cai, Z.; Guest, J.R.; Ren, Y.; Stamenkovic, V.; Curtiss, L.A.; Liu, Y.; Rajh, T.; *Nature Energy* **2019** 4:11, **2019**, 4, 957–968.
34. Kumar, S.; Bhawna, N.; Gupta, A.; Kumar, R.; Bharti, A.; Kumar, A.; Kumar, V.; *Journal of Physical Chemistry C*, **2023**, 127, 7095–7106.
35. Ong, C.B.; Ng, L.Y.; Mohammad, A.W.; *Renewable and Sustainable Energy Reviews*, **2018**, 81, 536–551.
36. Raza, W.; Faissal, S.M.; Owais, M.; Bahnmann, D.; Muneer, M.; *RSC Adv*, **2016**, 6, 78335–78350.
37. Mirzaeifard, Z.; Shariatnia, Z.; Jourshabani, M.; Rezaei Darvishi, S.M.; *Ind Eng Chem Res*, **2020**, 59, 15894–15911.
38. Janani, B.; Syed, A.; Hari Kumar, B.; Elgorban, A.M.; Bahkali, A.H.; Ahmed, B.; Das, A.; Sudheer Khan, S.; *Opt Mater (Amst)*, **2021**, 120, 111438.
39. Tzompantzi, F.; Piña, Y.; Mantilla, A.; Aguilar-Martínez, O.; Galindo-Hernández, F.; Bokhimi, X.; Barrera, A.; *Catal Today*, **2014**, 220–222, 49–55.
40. Anucha, C.B.; Altin, I.; Bacaksiz, E.; Stathopoulos, V.N.; *Chemical Engineering Journal Advances*, **2022**, 10, 100262.
41. Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnmann, D.W.; *Chem Rev*, **2014**, 114, 9919–9986.
42. Malathi, A.; Madhavan, J.; Ashokkumar, M.; Arunachalam, P.; *Appl Catal A Gen*, **2018**, 555, 47–74.
43. Chen, S.H.; Jiang, Y.S.; Lin, H.Y.; *ACS Omega*, **2020**, 5, 8927–8933.
44. Ong, W.J.; Tan, L.L.; Ng, Y.H.; Yong, S.T.; Chai, S.P.; *Chem Rev*, **2016**, 116, 7159–7329.
45. Paul, D.R.; Gautam, S.; Panchal, P.; Nehra, S.P.; Choudhary, P.; Sharma, A.; *ACS Omega*, **2020**, 5, 3828–3838.
46. Sujatha, G.; Shanthakumar, S.; Chiampo, F. *Environments - MDPI*, **2020**, 7, 1–13.
47. Nasikhudin; Diantoro, M.; Kusumaatmaja, A.; Triyana, K.; *Journal of Physics: Conference Series*, **2018**, 1011, 012069.
48. Khlyustova, A.; Sirotkin, N.; Kusova, T.; Kraev, A.; Titov, V.; Agafonov, A.; *Mater Adv*, **2020**, 1, 1193–1201.
49. Ohko, Y.; Ando, I.; Niwa, C.; Tatsuma, T.; Yamamura, T.; Nakashima, T.; Kubota, Y.; Fujishima, A. *Environ Sci Technol*, **2001**, 35, 2365–2368.
50. Venkatachalam, N.; Palanichamy, M.; Murugesan, V. *Mater Chem Phys*, **2007**, 104, 454–459.
51. Karami, A.; *Journal of the Iranian Chemical Society*, **2010**, 7, S154–S160.
52. Bian, Z.; Zhu, J.; Li, H.; *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, **2016**, 28, 72–86.
53. Yin, H.; Wada, Y.; Kitamura, T.; Kambe, S.; Murasawa, S.; Mori, H.; Sakata, T.; Yanagida, S.; *J Mater Chem*, **2001**, 11, 1694–1703.
54. Kim, S.J.; Park, S.D.; Jeong, Y.H.; Park, S.; *Journal of the American Ceramic Society*, **1999**, 82, 927–932.
55. Abou-Helal, M.O.; Seeber, W.T.; *Appl Surf Sci*, **2002**, 195, 53–62.
56. Mills, A.; Elliott, N.; Parkin, I.P.; O'Neill, S.A.; Clark, R.J.; *J Photochem Photobiol A Chem*, **2002**, 151, 171–179.
57. Kim, D.S.; Kwak, S.Y.; *Appl Catal A Gen*, **2007**, 323, 110–118.
58. Tian, C.; *Scientific Reports* **2022** 12:1, **2022**, 12, 1–12.
59. Li, J.; Wan, W.; Zhou, H.; Li, J.; Xu, D.; *Chemical Communications*, **2011**, 47, 3439–3441.
60. Mamaghani, A. H.; Haghighat, F.; Lee, C. S.; *Chemosphere*, **2019**, 219, 804–825.
61. Kontos, A.I.; Arabatzis, I.M.; Tsoukleris, D.S.; Kontos, A.G.; Bernard, M.C.; Petrakis, D.E.; Falaras, P.; *Catal Today*, **2005**, 101, 275–281.
62. Testino, A.; Renato Bellobono, I.; Buscaglia, V.; Canevali, C.; D'Arienzo, M.; Polizzi, S.; Scotti, R.; Morazzoni, F.; *J Am Chem Soc*, **2007**, 129, 3564–3575.
63. Lu, C.-H.; Wu, W.-H.; Kale, R.B.; *J Hazard Mater*, **2008**, 154, 649–654.
64. Tao, J.; Zhang, M.; Lv, J.; Shi, S.; Gong, Z.; Yao, G.; Cheng, Y.; He, G.; Chen, X.; Sun, Z.; *Sci Adv Mater*, **2016**, 8, 941–947.
65. Akyol, A.; Yatmaz, H.C.; Bayramoglu, M.; *Appl Catal B*, **2004**, 54, 19–24.
66. Begum, S.; Naik, N.D.; Solapure, R.B.; Sampate, G.G.; Salunke, A.P.; Narwade, V.N.; Dadge, J.W.; Danková, Z.; Mahabole, M.P.; Bogle, K.A.; *AIP Conf Proc*, **2020**, 2220.
67. Shirke, B. S.; Korake, P. V.; Hankare, P. P.; Bamane, S. R.; Garadkar, K. M.; *Journal of Materials Science: Materials in Electronics*, **2011**, 22, 821–824.
68. Theivasanthi, T.; Alagar, M.; *arXiv preprint arXiv*, **2013**, 1307.1091.
69. Delekar, S.D.; Yadav, H.M.; Achary, S.N.; Meena, S.S.; Pawar, S.H.; *Appl Surf Sci*, **2012**, 263, 536–545.
70. Taha, S.; Begum, S.; Narwade, V.N.; Halge, D.; Dadge, J.W.; Mahabole, M.P.; Khairnar, R.S.; Bogle, K.A.; *AIP Conf Proc*, **2020**, 2220.
71. Hossain, M. S.; Ahmed, S.; *Results in Materials*, **2023**, 20, 100492.

72. Mamaghani, A.H.; Haghighat, F.; Lee, C.S.; *J Photochem Photobiol A Chem*, **2019**, 378, 156–170.
73. Barba-Nieto, I.; Caudillo-Flores, U.; Fernández-García, M.; Kubacka, A.; *Molecules*, **2020**, 25.
74. Yoon, H.; Kim, D.; Park, M.; Kim, J.; Kim, J.; Srituravanich, W.; Shin, B.; Jung, Y.; Jeon, S.; *Journal of Physical Chemistry C*, **2018**, 122, 12114–12121.
75. Makula, P.; Pacia, M.; Macyk, W.; *Journal of Physical Chemistry Letters*, **2018**, 9, 6814–6817.
76. Enesca, A.; Isac, L.; *Materials*, **2020**, 13.
77. Vasiljevic, Z.Z.; Dojcinovic, M.P.; Vujanecic, J.D.; Jankovic-Castvan, I.; Ognjanovic, M.; Tadic, N.B.; Stojadinovic, S.; Brankovic, G.O.; Nikolic, M. V.; *R Soc Open Sci*, **2020**, 7.



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