

TiO₂/ZnO Nanocomposite Material for Efficient Degradation of Methylene Blue

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In this research work, we have produced a composite material consisting titanium dioxide (TiO₂) and zinc oxide (ZnO) nanostructures via precipitation method. Scanning electron microscopy (SEM) study has shown the mixture of nanostructures consisting nanorods and nano flower. Energy dispersive spectroscopy (EDS) study has confirmed the presence of Ti, Zn and O as main elements in the composite. X-ray diffraction (XRD) study has revealed that the successful presence of TiO₂ and ZnO in the composite. The composite material exhibits small optical energy band gap which led to reduction of the charge recombination rate of electron–hole pairs. The band gap for the composite TiO₂/ZnO samples namely 1, 2, 3 and 4 is 3.18, 3.00, 2.97 and 2.83 eV respectively. Small optical bandgap gives less relaxation time for the recombination of electron and hole pairs, thus favorable photodegradation is found. The degradation efficiency for the TiO₂/ZnO samples for methylene blue in order of 55.03%, 75.7%, 85.14% and 90.08% is found for the samples 1, 2, 3 and 4 respectively. The proposed study of titanium dioxide addition into ZnO is facile and inexpensive for the development of efficient photocatalysts. This can be capitalized at large scale for the energy and environmental applications.

Keywords: Titanium Dioxide, ZnO, Methylene Blue, Degradation Efficiency.

1. INTRODUCTION

Water is known as an essential element of life and it has been polluted with variety of pollutants due to the industrialization and it is regarded as the most problem for the sustainability of healthy life on the earth planet [1–3]. Furthermore, as the global population is expected to increase within the next 50 years and consequently a huge need of safe and clean water is unavoidable [4]. In 2002, the World Health Organization reported that out of 6 people have limited access to clean water. And 2.6 billion people are lacking with basic sanitation amenities which causes

the death of approximately 4500 children per day [5]. The crisis of safe water is created by the people themselves by discarding the wastage into the water reservoirs. From pollution perspective, dyes and phenolic compounds are the hazardous pollutants. They are thrown as the wastage into the water through (textiles, foodstuffs and leather industries). These pollutants have adverse effects on the people and environment. These dyes are colored by nature, thus decreases the sunlight transmission, and photosynthesis process and are strongly problematic for the aquatic life. Moreover, these dyes are carcinogenic in nature and increase the number of undesirable products into the atmosphere [6, 7]. “According to the search engine of Web of

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Science, enormous amount of research activities around the globe is conducted on the photocatalysis, and the number of published articles is around 12400 in last five years.”

These research articles are mainly using the photocatalysis approach for the degradation of organic dyes, among them Methylene Blue (47%) and Methyl Orange (36%) are highly investigated [8]. The removal of these dyes from the wastewater is highly important for the healthy life and sustainable development [9]. Several methods are used for the treatment of wastewater such as chemical precipitation, electro-deposition, ion-exchange adsorption, filtration and membrane system and some of them have practicality. Despite the practicality of these methods, they are slow and do not degrade these chemically stable dyes. Also, these methods are limited at large scale and require expensive equipment [10]. However, the photocatalytic degradation and adsorption are promising methods for the elimination of organic pollutants from the water. The sun light is used in the photocatalysis for the degradation of organic dyes and it makes the degradation methodology more efficient and cheaper [11]. The photocatalytic degradation method requires photosensitive material which can be activated during the interaction of photons of light. The most investigated nanostructured materials include zinc oxide, tungsten trioxide, cadmium sulfide, zinc sulfide, strontium titanite, silver nanoparticles, ferric oxide, and titanium dioxide for the degradation of organic compounds [12, 13]. Titanium dioxide (TiO₂) is extensively used for the degradation of organic pollutants for two decades. It possesses unique and attractive properties such as super hydrophilicity and low cost [14–17].

Due to wide band gap of TiO₂ approximately 3.1 eV its photoconversion efficiency in aquatic solution for the degradation of dyes is poor and it only uses UV portion of sunlight for the photodegradation which is 4% of light. Therefore, novel and functional materials are needed to realize the photodegradation technology for the practical applications. In addition to TiO₂, ZnO, SnO₂ and WO₃ [18] are also studied for the photodegradation, among them ZnO is found as promising material for the replacement of TiO₂, it has also limited photodegradation activity due to its wide band gap and fast charge recombination rate. Further improving the efficiency of ZnO, doping strategy is one way by which band gap of ZnO can be tuned. Therefore, ZnO has been doped with different metals such as Al [19], Cu [20], Ga [21–27] etc. The mechanical strategy for the synthesis of TiO₂/ZnO as composite material is rarely investigated for the improved photodegradation efficiency. The composite has not only the low optical bandgap, but it induces the double effect on degradation from both ZnO and TiO₂ at the same time. The titanium dioxide influenced on the optical band

gap of composite materials which needs more attention for photochemical applications and photodegradation efficiency.

In this study, we have produced a composite of TiO₂ and ZnO by precipitation method. The TiO₂/ZnO nanostructures are characterized by various analytical techniques such as SEM, EDS and XRD. The TiO₂/ZnO nanostructures are employed for the degradation of methylene blue in aquatic solution and more than 90% degradation efficiency is recorded. The proposed photocatalyst can be used for the wide range of photochemical applications such as water splitting and solar cells etc.

2. MATERIALS AND METHODS

Titanium dioxide bulk powder (TiO₂, $M = 79.866$, Merck), zinc acetate-dihydrate (ZnC₄H₆O₄, $M = 183.48$, Merck), ammonia solution (25%, Merck), methylene blue, and ethanol (C₂H₅OH, 99.5% were purchased from (Sigma–Aldrich) and used without further purification.

2.1. Synthesis of TiO₂ and ZnO Composite by Precipitation Method

The synthesis of TiO₂ and ZnO photocatalysts was followed by the precipitation method. In a typical synthesis, zinc acetate-dihydrate (ZnC₄H₆O₄, $M = 183.48$, Merck) and ammonia solution (25%, Merck) were used as primary precursors. The procedure for the preparation of TiO₂ and ZnO composite was as followed: (i) firstly different amounts of titanium dioxide bulk powder such as 5, 10, 15 and 20 mg was mixed in 5 mL of ethanol (C₂H₅OH, 99.5%) separately through sonication until a homogenous mixture was obtained (ii) then 4 separate beakers containing 5 mL of 25% ammonia and 2.22 g of zinc acetate-dihydrate (ZnC₄H₆O₄, $M = 183.48$, Merck) as primary precursor and 100 mL of DI water were set: (iii) after that, 5 mg, 10 mg, 15 mg and 20 mg TiO₂ powder dispersed into 5 mL ethanol was added into the zinc and ammonia precursor. The samples of TiO₂ and ZnO with 5, 10, 15 and 20 mg TiO₂ were labeled as sample 1, 2, 3 and 4 respectively. (v) Finally, the beakers were tightly covered with aluminum foil in order to avoid the spoilage of growth solution and kept in electric oven at 90 °C for 5 h. Afterwards, white powder settled at the bottom of each beaker and it was collected by filtration using common filter paper and washed with the deionized water DI water, and dried in an oven for overnight at 60 °C. The pristine ZnO nanostructures without addition of TiO₂ were prepared by same methodology.

2.2. Characterization Techniques

The powder X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) were used to study the crystal structure, morphology and composition of as prepared nanostructured ZnO.

2.3. Photocatalytic Activity Measurement of as Prepared ZnO Nanostructures

The photocatalytic measurement was performed with the illumination of UV light in a homemade photo reactor using pristine ZnO, and samples 1, 2, 3, and 4. The 5 mg of each photocatalyst was used in the 100 mL of aqueous solution of MB dye (50 mg/L) and solution was stirred for 5 min. Then the mixture was exposed to UV light having power of 15 W, 220 V and 60 Hz frequency as UV source and positioned parallel to reactor. UV-Vis spectrophotometer (Evolution 300 UV-Vis, Thermo fisher Scientific) was used for monitoring the degradation rate of MB.

The percentage degradation of MB was estimated by the following relation:

$$\% \text{ degradation} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Here C_o is the initial absorbance of dye, C_t is the absorbance of dye at time “ t ”.

2.4. Kinetics of Dye Degradation

The degradation kinetics was calculated using Langmuir-Hinshelwood model [28, 29].

$$r = -\frac{dC_t}{dt} = k\theta = \frac{kK C_t}{1 + K C_t} \quad (2)$$

Here r is the degradation rate (mg L⁻¹ min⁻¹) t is the time (min), k is the degradation rate constant (mg L⁻¹ min⁻¹), s is the fractional coverage of catalyst surface, and K is the adsorption equilibrium constant (L mg⁻¹).

It has been shown that a weak adsorption or low reactant concentration ($K C_t \ll 1$), Eq. (2) can be assigned to a pseudo-first order kinetic

$$\frac{dC_t}{dt} = k K C_t = -K_{app} C_t$$

Here rate constant is K_{app} apparent rate constant (min⁻¹). By integrating Eq. (4) gives

$$\ln\left(\frac{C_t}{C_o}\right) = -K_{app} t$$

Therefore, the measured value of K_{app} can be drawn from the slope of a plot $\ln(C_t/C_o)$ versus t .

3. RESULTS AND DISCUSSION

The crystallographic study has shown well resolved diffraction patterns for pristine ZnO, bulk TiO₂ and their mixture as shown in Figure 1. The diffraction patterns recorded for pristine ZnO are 31.737° (010), 34.420° (002), 36.225° (011), 47.515° (012), 56.536° (220), 62.836° (002), 66.304° (020), 67.893° (112), 69.015° (221), 72.561° (112) and 76.891° (131) and they are well matched to standard JCPDS card no. 96-900-4182 and

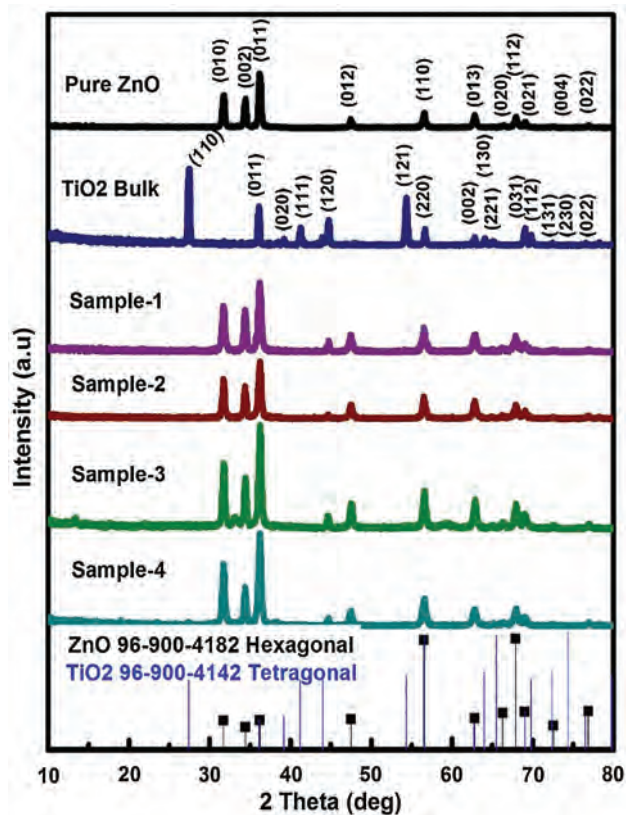


Figure 1. XRD patterns of pristine ZnO and TiO₂/ZnO samples 1, 2, 3, and 4.

belongs to wurtzite hexagonal phase of ZnO. However, samples of TiO₂. ZnO composite has shown weak TiO₂ reflections which are found at 27.440°(110), 36.079°(011), 39.197°(020), 41.240°(111), 44.050°(120), 54.325°(121), 56.635°(220), 62.752°(002), 64.058°(130), 65.517°(221),

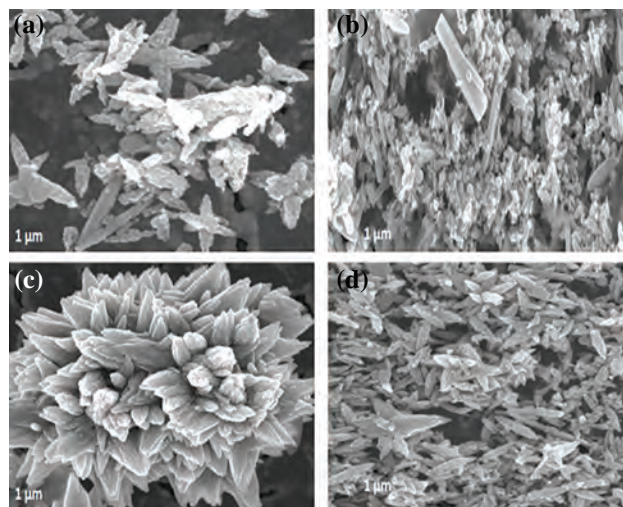


Figure 2. (a–d) Typical FESEM images of prepared TiO₂/ZnO nanostructures (S1–S4).

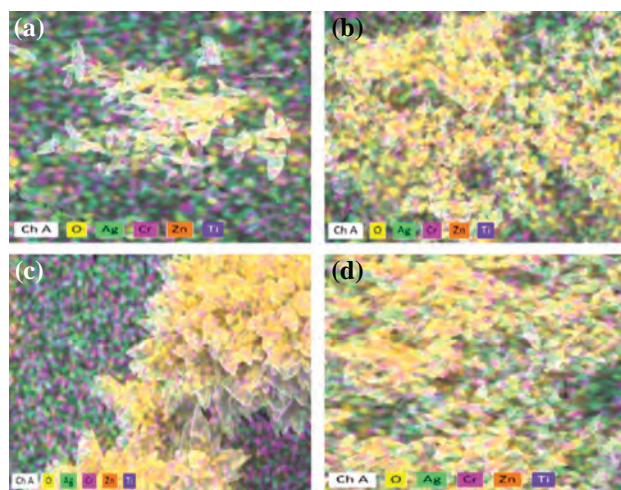


Figure 3. Elemental mapping of different TiO₂/ZnO nanostructures sample 1 (a) sample 2 (b) sample 3 (c) and sample 4 (d).

69.012°(031), 69.797°(112), 72.427°(131), 74.414°(230) and 76.536°(022) and they are in good agreement with the standard JCPDS card no. 96-900-4142 and indexed to rutile phase of bulk TiO₂. XRD study has confirmed the presence of TiO₂ and ZnO phases in the composite. We found rutile and hexagonal phases of TiO₂ and ZnO in the composite samples 1–4. No other phase or impurity was detected by XRD measurement.

The shape and surface information were collected from the SEM analysis as depicted in Figure 2. The TiO₂/ZnO samples have shown the mixture of morphologies consisting predominantly flower in the structure. The alteration

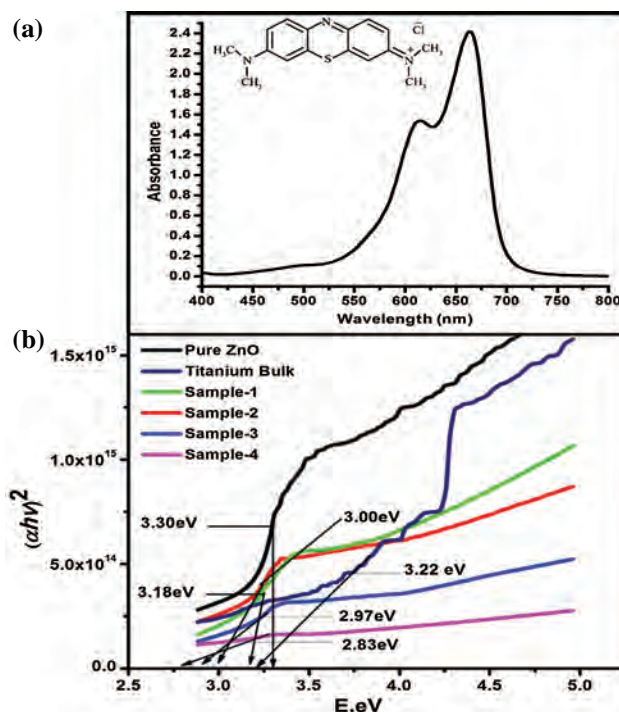


Figure 5. (a) UV-Visible absorption spectra of MB (b) Tauc plots for the pristine ZnO and TiO₂/ZnO.

in the morphology could be assigned to the presence of ethanol in the growth solution, thus a shift in the structure from nanorods to flowers is resulted. The length of nanostructures is few microns and diameter in between 200 to 300 nm. Figure 3 shows the elemental mapping spectra of

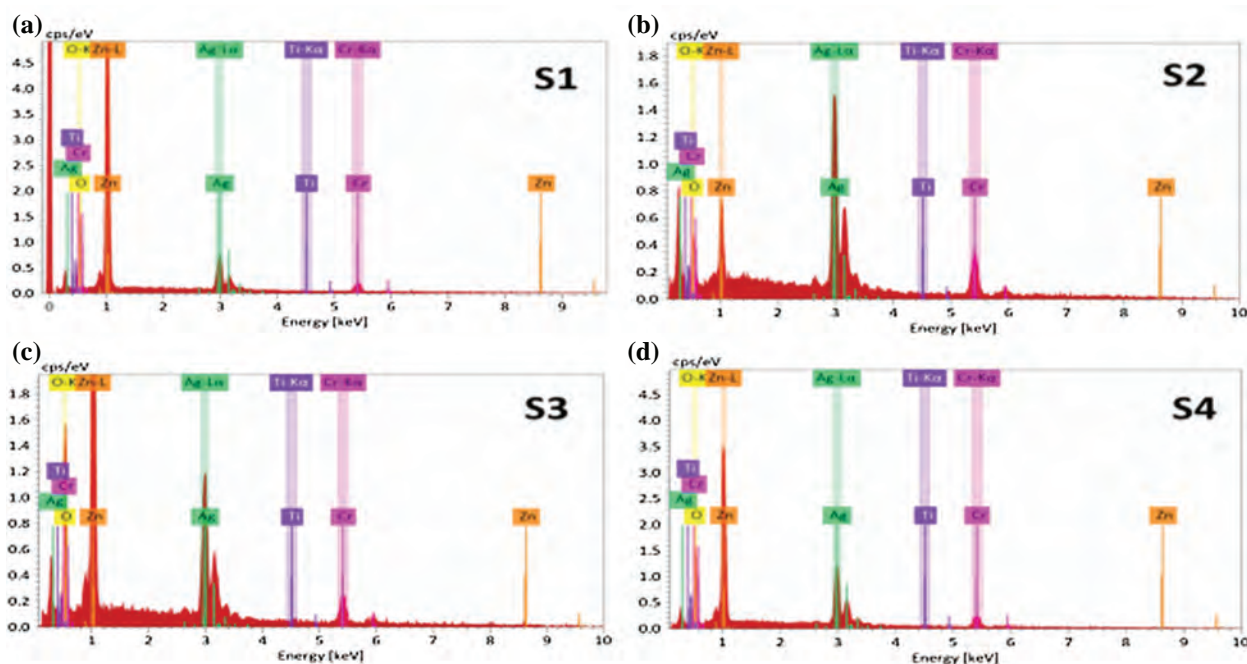


Figure 4. EDX spectrum of TiO₂/ZnO nanostructures sample 1 (a) sample 2 (b) sample 3 (c) and sample 4 (d).

EDS and it confirms the composition of TiO₂/ZnO samples and the Ti, Zn and O are the main elements in the composite samples as enclosed in Figure 4.

3.1. Photocatalytic Degradation of Methylene Blue MB Dye Using Various TiO₂/ZnO Composites

The proposed mechanism for the photodegradation is shown in Figure 9. Furthermore, the photodegradation mechanism of MB on the TiO₂/ZnO samples can be described as: The conducting band electrons of titanium dioxide during the interaction of UV might have equal or greater energy than the optical band gap of ZnO and the electrons from the conducting band of titanium dioxide and are excited towards the conduction band of ZnO and at the same time, equal number of holes in the valence band of ZnO are created which moves towards valence band of titanium dioxide as shown in Figure 9. The adsorption of titanium dioxide particles on the surface of ZnO nanostructures helps to trap electrons and prevent the electron and hole recombination, thus leading to the excellent photocatalytic activity. Also, there is possibility of excitation of MB molecules by irradiation of UV light which could favor the rapid and efficient photodegradation

of MB. Prior to the degradation of MB, the absorption spectrum of bare MB was recorded as shown in Figure 5(a) and inset shows the molecular structure of MB. From molecular structure it is seen that MB is cationic dye and has absorption around 663 nm [30]. The UV-visible spectroscopy was used to investigate the optical properties of TiO₂/ZnO samples and pristine ZnO. The absorption spectra are shown for the wavelength of 230–450 nm for the calculation of optical band gap. The absorption spectra indicate the sharp peaks below 400 nm for all samples as shown in Figure 5(a). Pathak et al. [31] has described that ZnO has absorption below 400 nm and Li et al. [32] also found that absorption edge for the TiO₂ is close to 400 nm. We have also found the absorption edges close to 350–400 nm for all these samples. This is in good agreement for the optical band gap of TiO₂/ZnO samples. In the absorption edge a red shift is seen for the higher content of TiO₂ in the composite sample. Importantly, the composite is a physical mixture of two materials and possibly weak forces are present. We collected the UV-visible spectra for both materials in each sample thus it might change the absorption window that further reduced the band gap for the composite materials.

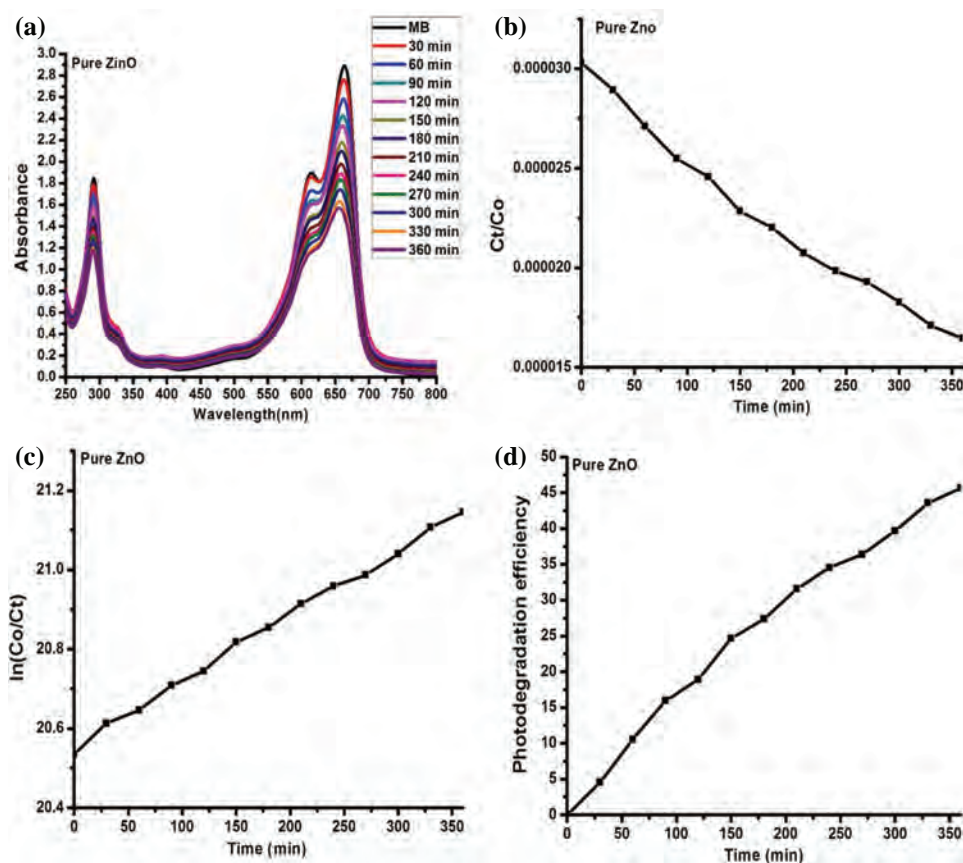


Figure 6. (a) Shows photocatalytic degradation of MB dye solution under UV light in the presence of pristine ZnO at different time; (b) Photocatalytic decolonization kinetics of MB using pristine ZnO as a photocatalyst; (c) Kinetic plot of $\ln(Co/Ct)$ versus irradiation time for photodegradation of pristine ZnO and (d) Photo degradation efficiency (%) versus different intervals of time for the pristine ZnO.

The variation in the photocatalytic activity can be attributed from the particle size, surface structure and the amount of TiO₂ and ZnO in the composite samples. Figure 5(b) describes the optical band gap of pristine ZnO and TiO₂/ZnO composite which is seen from the Tauc plot. The optical band gap for the pristine ZnO is 3.30 eV and for the TiO₂/ZnO samples 1, 2, 3 and 4 is 3.18, 3.00, 2.97 and 2.83 eV respectively. The optical bandgap of bulk TiO₂ was found around 3.2 eV which is nearly close to the optical bandgap of TiO₂ 3.1 eV reported elsewhere. This indicates that the addition of TiO₂ causes the alteration of optical band gap of composite samples. Based on the optical bandgap, the photodegradation mechanism for methylene blue can be explained as: The small band gap provides less relaxation time for the recombination electron and hole pairs, thus favorable photodegradation is observed for the sample. However, large optical band gap shows a more relaxation time for the interaction of electron and hole pairs, consequently enhanced recombination rate is unavoidable. Therefore, poor degradation efficiency is demonstrated by the pristine ZnO with optical band gap of 3.30 eV. Figure 6 shows the photodegradation efficiency of pristine ZnO which has shown relatively poor efficiency of 45.68% for the MB. The poor performance of pristine ZnO nanostructures for the degradation of MB

is attributed to the fast charge recombination rate and wide band gap. Figure 7 shows the UV-Visible absorption spectra of MB dye for the TiO₂/ZnO nanostructures. It can be seen that the degradation depends on the irradiation time and amount of TiO₂, ZnO nanostructures which can be observed through the decline in the absorption peak at 663 nm. The degradation efficiency for the TiO₂/ZnO samples is in order of 55.03%, 75.7%, 85.14% and 90.08% degradation in 220 min under UV light irradiation for the samples 1, 2, 3 and 4. Larger amount of TiO₂ led to rapid and higher degradation efficiency, thus the prepared photocatalysts are highly sensitive to degradation of MB, particularly sample 4.

Figure 8(a) shows the plot of C/C₀ versus time which shows the reduction in concentration of methylene blue (MB) dye for the TiO₂/ZnO samples. Figure 8(b) shows ln(C/C₀) versus irradiation time which indicates the pseudo first order kinetics and extracting the slope from graph can be assigned to the rate constant. Obviously, higher the value of rate constant, more favorable will be the kinetics of photodegradation of MB. Figure 8(c) shows the % degradation of MB dye TiO₂/ZnO nanostructures. It can be found that photodegradation efficiency is higher for sample 3 and 4 which is 85.14% and 90.08% respectively in 220 min under UV light irradiation.

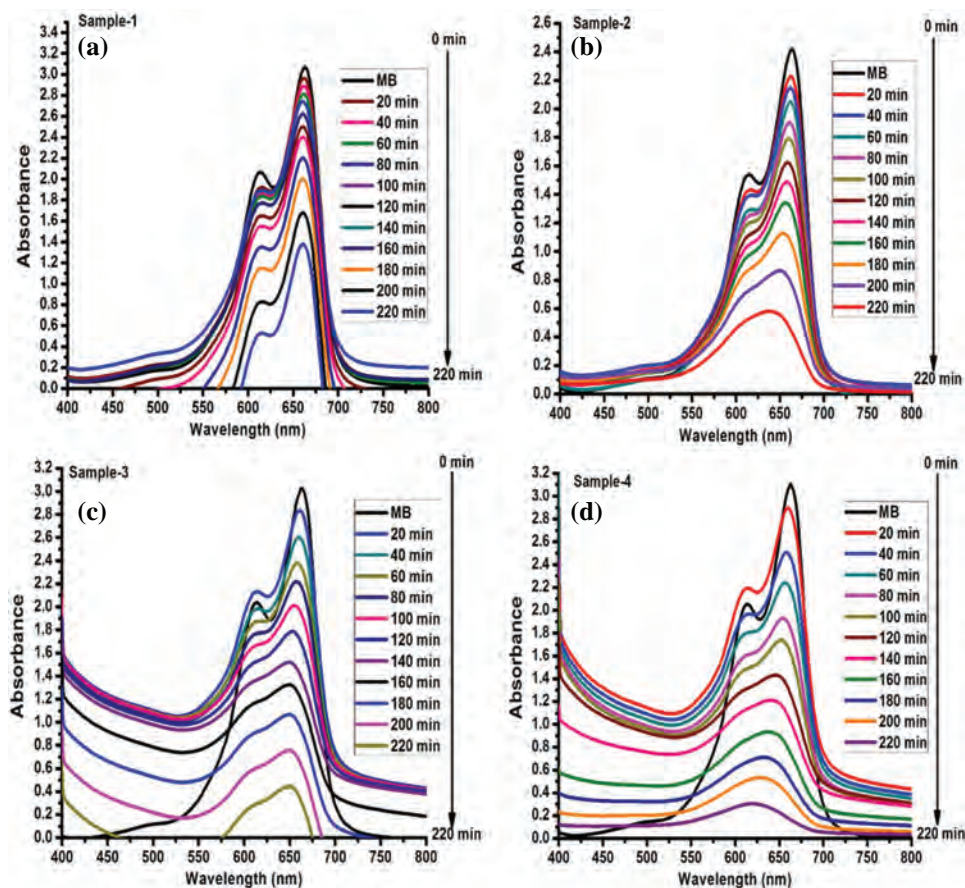


Figure 7. (a–d) Time-dependent UV-Vis absorption spectra for MB dye solution after irradiation of UV-light for samples 1, 2, 3, and 4.

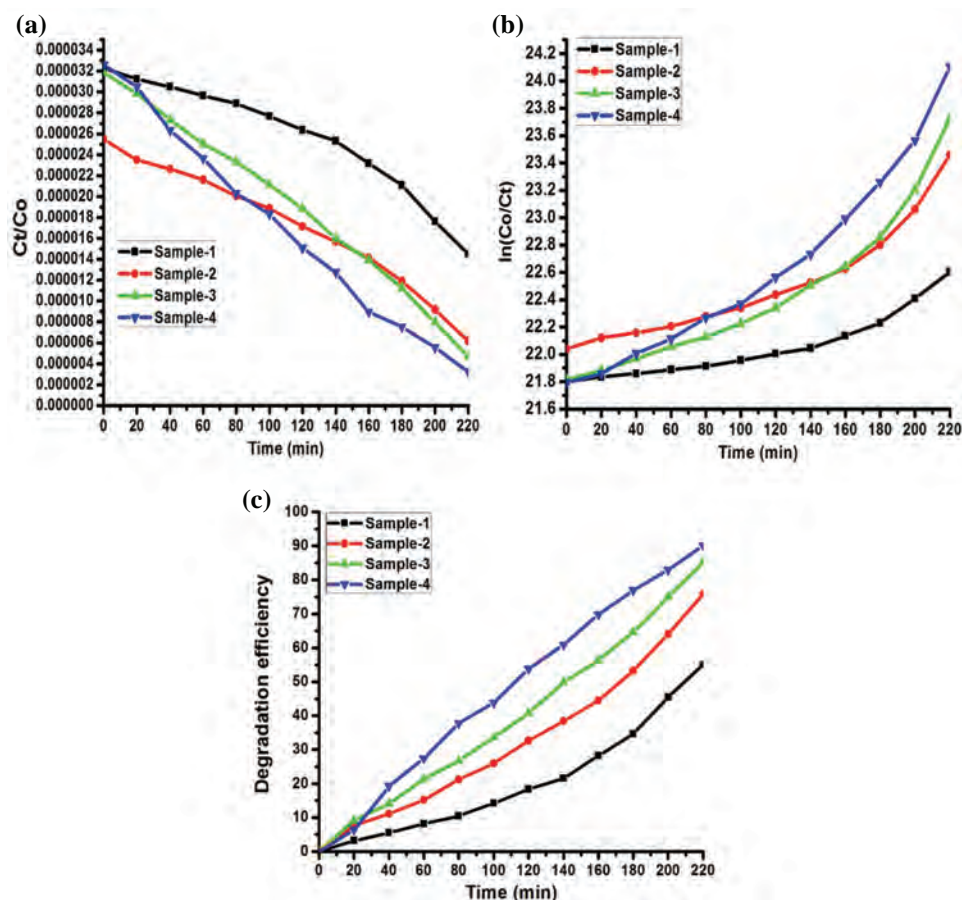


Figure 8. (a) C/C_0 versus time curves of MB for the samples 1, 2, 3 and 4; (b) shows the Kinetic plot of $\ln(C_0/C_t)$ versus irradiation time for the samples 1, 2, 3 and 4 and (c) shows % degradation rate versus different time intervals for the samples 1, 2, 3 and 4.

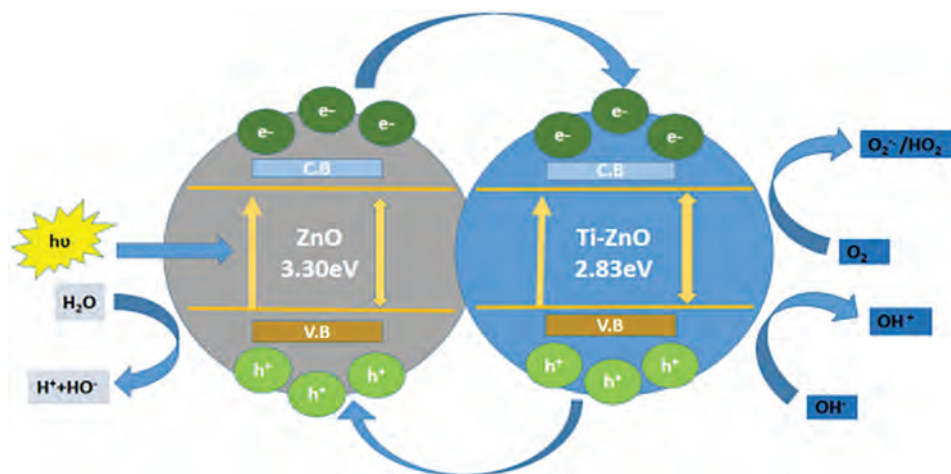


Figure 9. Proposed mechanism of photodegradation using TiO₂/ZnO composite.

4. CONCLUSION

Tailoring the band gap of ZnO using mechanical strategy by combining with bulk TiO₂ using precipitation method is presented. The addition of TiO₂ in the composite samples has decreased its optical band gap and consequently

reduced relaxation time for the interaction of electron and hole pairs, this further led to decrease in recombination rate and it paved the way towards an efficient degradation of methylene blue. The different amount of TiO₂ is introduced in the composite samples. The degradation

efficiency for the TiO₂/ZnO samples is in order of 55.03%, 75.7%, 85.14% and 90.08% degradation in 220 min under UV light irradiation for the samples 1, 2, 3 and 4 respectively. This study provides inexpensive, earth abundant and functional photocatalyst materials for the realization of practical energy and environmental applications.

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