CSVTU Research Journal

Vol. 10(1), 01–13 2021 ISSN: 0974-8725

Research Article

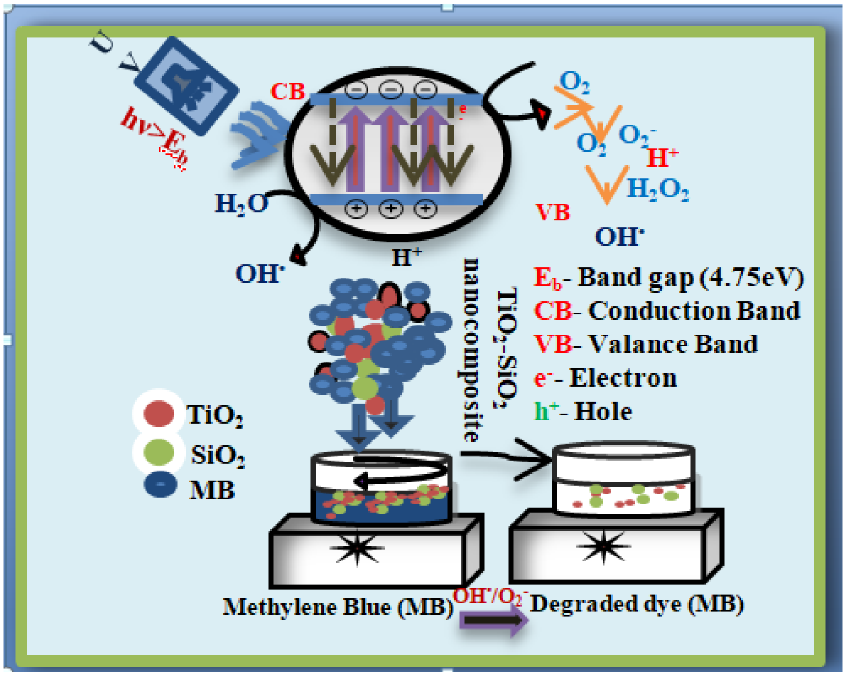
Synthesis of TiO_2-SiO_2 nanocomposite by sol-gel method for photocatalytic removal of dye: potential application for dye industry

Amiya Kumar Jana, Priyankari Bhattacharya, Sathi Banerjee
Department of Metallurgical and Materials Engineering, Jadavpur University, Kolkata 700032, India,
Corresponding author: sathibanerjeeju@gmail.com

Received February 21, 2021; received in revised form April 1, 2021; Accepted April 15, 2021, Published August, 2021

Research Highlights

1. Room temperature synthesis of TiO_2-SiO_2 by sol-gel route.
2. 100% anatase form of TiO_2 has been achieved with mean crystallites size 6.42nm.
3. This nanocomposite shows better photocatalytic activity as compare to commercially available pure TiO_2 for same duration of time (dark adsorption and UV-irradiation) and dye concentration.
4. This composite can degrade around 95% of dye up to 50ppm dye concentration with in 30min (20min adsorption and 10min UV-irradiation).



Graphical abstract

ABSTRACT

Sol-Gel technique was employed to synthesize TiO_2-SiO_2 nanocomposites using Titanium (IV) isopropoxide (TTIP) as a precursor of TiO_2 in acidic pH. Silica sol was prepared using Tetraethyl orthosilicate (TEOS) and mixed with Titania solution. HNO_3 was used as a peptizing agent. Gel formation was obtained at room temperature followed by drying at 100°C and calcination at four different temperatures viz. 500°C, 550°C, 600°C and 700°C. The mean crystallite size of the particles was calculated from X-ray diffraction using Scherrer's equation. Samples calcined at 550°C, showed minimum mean crystallite size (6.42nm). Surface morphology was observed from Field emission scanning electron microscopy. Fourier-transform infrared spectroscopy spectra confirmed the existence of Ti-O-Ti, Si-O-Si and Si-O-Ti bond. Methylene blue was used as model dye for observing photocatalytic activity of nanocomposite material. About 99% dye removal was obtained after 20 min of adsorption and 10 min of UV-irradiation using 70:30 ratio of TiO_2: SiO_2 nanocomposite (2g/L).

Keywords: composites; oxides semiconductors; Sol-gel; optical properties; X-ray diffraction

1. Introduction

Titanium dioxide (TiO_2) nanomaterial bears some unique properties which drawn attention of many researchers over the decade. Various applications of this nanomaterial include waste water treatment, environmental purification, optoelectronic devices, photo-electrochemical solar energy conversion and hydrophilic coating and etc. [1-6]. Especially properties like environment friendly, chemical stability, non-toxicity and photo activity of TiO_2 makes its widespread industrial wastewater treatment [7]-[9]. Among three crystalline phases of TiO_2 viz. anatase, brookite and rutile; anatase phase is mostly studied in photo degradation because of its larger specific surface area, larger band gap energy. Although anatase TiO_2 shows very good photocatalytic activity owing to its greater surface area and band gap energy but their commercial applications are impeded due to the various reasons. Agglomeration of very fine powders in reaction system results in formation of larger particles that decreases catalytic performance. Thus, the separation or recovery of those ultra-fine nano particles becomes very difficult and costly. Moreover, larger agglomerated particles result in weaker adsorption. Lastly, the material is active only under UV light because of large band gap energy (3.2eV). Under normal sunray it results approximately 4% absorption only which considered to be very less [10]. Several efforts have been given to overcome those barriers and to develop modified TiO_2 catalyst, which can offer better adsorption, lower band gap energy, effective and stable surface area as well as easy to separate from aqueous solution [11]-[13].

The modification of TiO_2 can be done in several ways. Many researchers have tried many different techniques via several synthesis routes. Ternary TiO_2-SiO_2-Ag nanocomposites was synthesized through a facile biomimetic approach by utilizing lysozyme as both inducing agent of TiO_2 and reducing agent of Ag+ to enhance visible-light photocatalytic activity [14]. Sharma and Lee (2016) have found better photocatalytic activity of TiO_2-MgO nanocomposite synthesized via sol-gel process, than pure TiO_2 under visible light [15]. Another synthesis method i.e. supercritical fluid combination technique was used by Wei and Zhang (2017) for synthesis of Fe_2O_3/TiO_2 nanocomposite. The study showed significant improvement in catalytic activity compared with pure TiO_2 [16]. Yan et.al (2012) observed that doping TiO_2 with rare earth metal like Cesium (Ce) via sol-gel route offers broader absorption region to visible light by inhibiting the recombination of the photo-generated electron hole pairs which results better photo catalytic activity [17].

Among the different metal oxide for synthesis of nanocomposite, silicon dioxide promises to be a good candidate as to combine with TiO_2. It offers different advantages over pure TiO_2 like it increases specific surface area caused by the presence of a network structure of SiO_2. This results in high adsorption of wide range of organic compounds, water, and hydroxyl molecules. TiO_2:SiO_2 mixed oxides show better structural and thermal stability [18]-[19]. Addition of silica could inhibit the charge carrier surface recombination, especially in small size particles [10]. Also, it increases the photocatalysis activity, even in darkness [20].

In this present work TiO_2:SiO_2 nanocomposite was prepared via sol-gel technique using titanium tetraisopropoxide (TTIP) as precursor of TiO_2 and tetraethyl orthosilicate (TEOS) as precursor of SiO_2. Prepared photocatalyst was characterized by XRD, FESEM, EDS, FTIR and UV-VIS. Photo activity of the catalyst was evaluated by using methylene blue (MB) dye under UV irradiation. Effects of dose, dye concentration, time etc. was observed for optimization of experimental parameters.

(i) Experimental

Materials

TiO_2-SiO_2 nanocomposite was prepared via sol-gel synthesis route using Titanium (IV) Isopropoxide (TTIP, Sigma-Aldrich, Germany) as precursor of TiO_2 and tetraethyl orthosilicate (TEOS, Sigma-Aldrich, Germany) as precursor of SiO_2. Nitric Acid (HNO_3, Merck, India) was used as peptizing agent in sol-gel reaction. For photocatalytic activity study Methylene Blue (Merck, India) was used as a model dye. All materials are of analytical grade.

Synthesis of TiO_2-SiO_2 nanocomposite

For synthesizing TiO_2:SiO_2 nano photo catalyst HNO_3: TTIP: Ethanol (solvent medium) was mixed in 1:2:4 ratios (Solution A). This mixture was stirred in magnetic stirrer for one hour at room temperature. In another beaker TEOS was mixed with ethanol and stirred for 30 min at room temperature (Solution B). Solution B was mixed drop wise to Solution A in magnetic stirrer at rotational speed of 700rpm. The mixture was put on a sonicator and 30ml of deionized water was added to it. Initial clear solution started to become hazy within 1 hour of sonication. It was allowed to age at room temperature for 48hrs. A thick gel was formed after 48hrs, which was dried at 100°C to obtain a brownish yellow powder. The powder was neutralized, dried and calcined at four different temperatures viz. 500°C, 550°C, 600°C and 700°C. Optimum calcination temperature was selected after the analysis of different characterizations results. Four different weight ratios of TiO_2-SiO_2 i.e. 60:40, 70:30, 80:20 and 90:10 were prepared and calcined at that particular temperature.

Characterization of prepared nanocomposite

The crystalline structure and phases of synthesized TiO_2–SiO_2 nanocomposites were analyzed using X-ray diffraction meter (XRD) (Model: D8 advance, Bruker AXS, Germany) at room temperature, operating at 40 kV and 30 mA, using Ni-filtered Cu- Kα radiation (λ= 0.15406 nm) and average crystal size was calculated by Scherrer’s formula. Functional groups of TiO_2–SiO_2 nanocomposites were determined using Fourier Transform Infrared spectroscopy (FTIR) spectra (Model: Shimadzu IRPrestige-21, Japan) with KBr pellet at a resolution of 4cm-1 and wave number ranging from 4000 cm-1 to 400 cm-1.

Band gap energy of the nanocomposite was evaluated using UV-Vis spectroscopy (Model: JASCO V-630 UV-Vis Spectrophotometer, UK) with wave number range of 800-200nm. Surface morphology of synthesized TiO_2–SiO_2 nanocomposites were characterized using Field Emission Scanning Electron Microscope (FE-SEM) (Model: Zeiss, SupraTM35VP, Oberkochen, Germany) operating with an accelerating voltage of 5kV. Elemental composition of the samples was analyzed using Energy Dispersive X-ray Spectroscopy (EDS) coupled with SEM (Model: Hitachi SU-8230 Japan) operating with an accelerating voltage of 20kV.

Photocatalytic experiments and analysis

Methylene Blue (MB) was used as model dye to study the photocatalytic activity of prepared nanocomposite. The local made photoreactor consisting of two 15Watt black fluorescent lamps, one magnetic stirrer and one exhaust fan was used for photocatalytic experiment.

Zeta potential test of performed nanocomposite shows surface potential value -4.46mv. As methylene blue (MB) is a basic dye in nature means it carries positive charge and attracted to the negatively charged surface. To make its surface more negative all samples were treated with NaOH (0.1N) solution [21]. Prior to photoactivity study all samples were ball milled in a high-speed ball milling machine to obtain fine powder.

To evaluate the photocatalytic performance following observations were made.

- Selection of the best ratio
- Effect of time on adsorption
- Effect of UV irradiation time
- Effect of variation of dose on dye degradation
- Effect of variation of dye concentration on dye degradation

For selection of the best ratio, experiment was performed on four different TiO_2: SiO_2 ratios i.e. 60:40, 70:30, 80:20, 90:10 and compared with commercially available pure TiO_2 nano powder (Sigma-Aldrich, Germany). The ratio which shows maximum degradation of dye was selected as the best ratio. For this purpose, 0.5gm TiO_2:SiO_2 catalyst (2g/L) was added into 250ml of 30ppm MB dye. Then solution was put on a magnetic stirrer with slow stirring speed for 30min dark adsorption followed by 15min UV irradiation. Samples were centrifuged and analyzed by UV-VIS to calculate degradation percentage.

Effect of time on adsorption and UV degradation was observed using three best ratios of TiO_2: SiO_2 from previous study viz. 70:30, 80:20 and 90:10 respectively using 2g/L dose and 30 ppm dye solution.

Adsorption study was conducted for 60 min and samples were drawn at regular intervals to observe colour change by UV-visible spectrometer. The dye solution was kept on a magnetic stirrer at 200rpm stirring speed for adsorption in dark condition.

The dye solution after adsorption was subjected to UV exposure for 30 min to observe the effect of time of UV on dye degradation. Samples were drawn at regular interval and subjected to spectrophotometric analysis to observe dye degradation.

Dose variation and dye concentration variation was performed on three different doses i.e. 1.5g/L, 2g/L and 2.5g/L, and at three different dye concentrations i.e.10ppm, 30ppm and 50ppm from above selected ratio and time. During all above experiment pH of the solution was fixed at 5.5.

3. Results and Discussion

3.1 Characterization of nanoparticles

XRD pattern of powder samples calcined at different temperature is shown in Fig. 1 (a). It was observed that only anatase phase of TiO_2 was prevalent in samples calcined at four different temperatures and SiO_2 is in amorphous form except for heat treated sample at 700°C (one peak of quartz (d_{203}) has been observed). Average crystallite size of all four samples heat treated at different temperatures was estimated from Scherrer's equation using the reflection of most intense anatase peak (101). The observed crystallite size (Table 1) matches with the reported value [10]. Addition of SiO_2 can reduce the growth rate of anatase in titania nanoparticle due to the Si atom, this agrees with the small value of crystallite size.

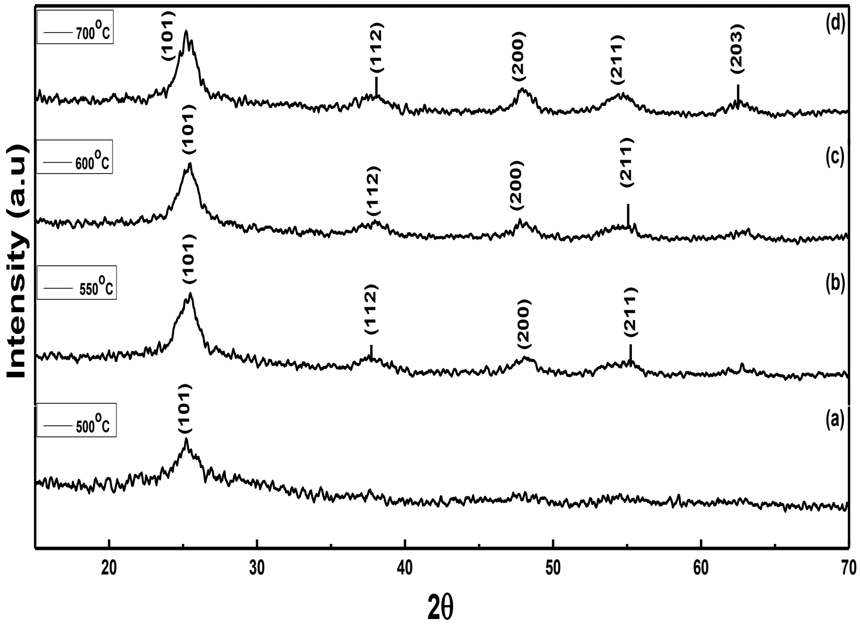


Fig 1 (a): XRD pattern of TiO2–SiO2 nanocomposites calcined at 500, 550, 600 and 700°C.

Table 1 Average crystallite size of TiO_2–SiO_2 nanocomposites calcined at different temperature.

Heating temperature (°C)	Average Crystallite Size (nm)
500°C	6.57
550°C	6.42
600°C	6.61
700°C	8.10

Samples calcined at 550°C showed minimum average crystallite size. As average crystallite size is directly related to grain size of nanomaterials, this sample will have minimum grain size compared to others. Minimum grain size indicates more surface area which means more available active sites for photocatalytic activity. So, all four batches of different weight ratios were prepared by calcined at 550°C for three hours at 5°C/min in a programmable tube furnace.

Fig. 1 (b) and (c) shows the FESEM image and EDS pattern of the sample calcined at 550°C. Careful observation of these FESEM images reveals that the surface of this nanocomposite has irregular morphology due to the agglomeration of primary particles, which may cause the surface to be non-uniform and inexplicit. The accumulation of primary particles indicates packed and dense structure. EDS analysis over random area reveals the existence of all three elements viz. Si, Ti and O indicating probable incorporation of TiO_2 in amorphous silicate framework to form nanocomposite.

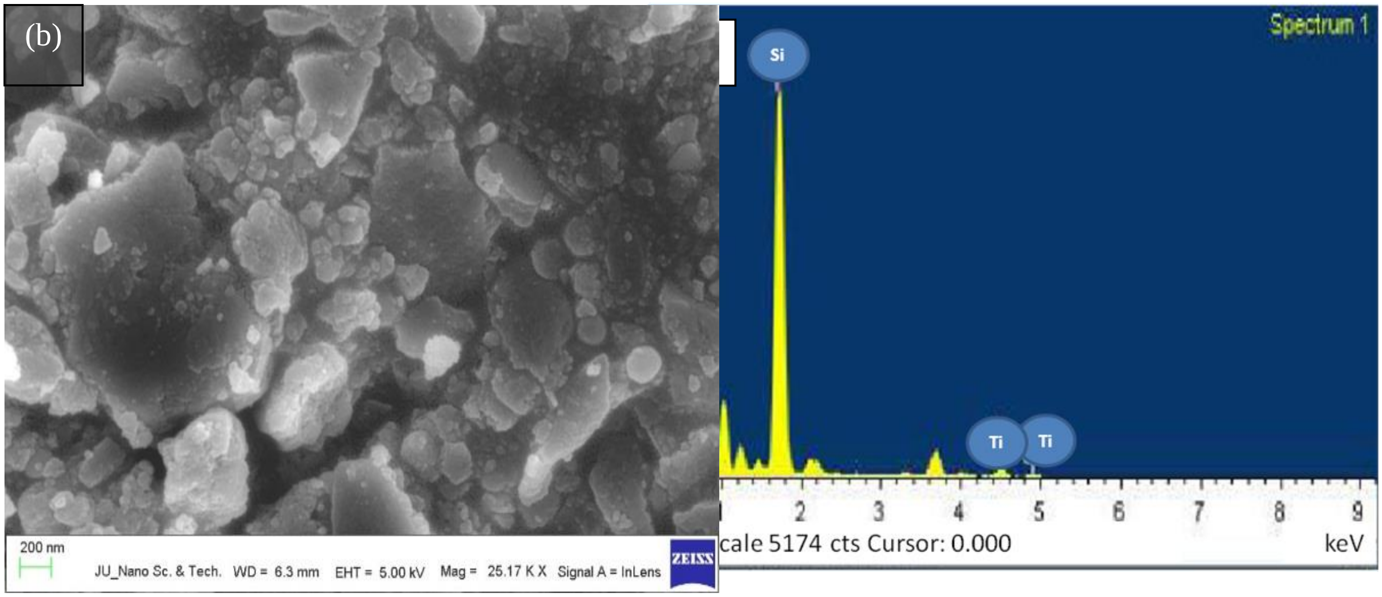


Fig 1: (b) FESEM image and (c) EDS pattern of TiO2-SiO2 nanocomposite calcined at 550°C.

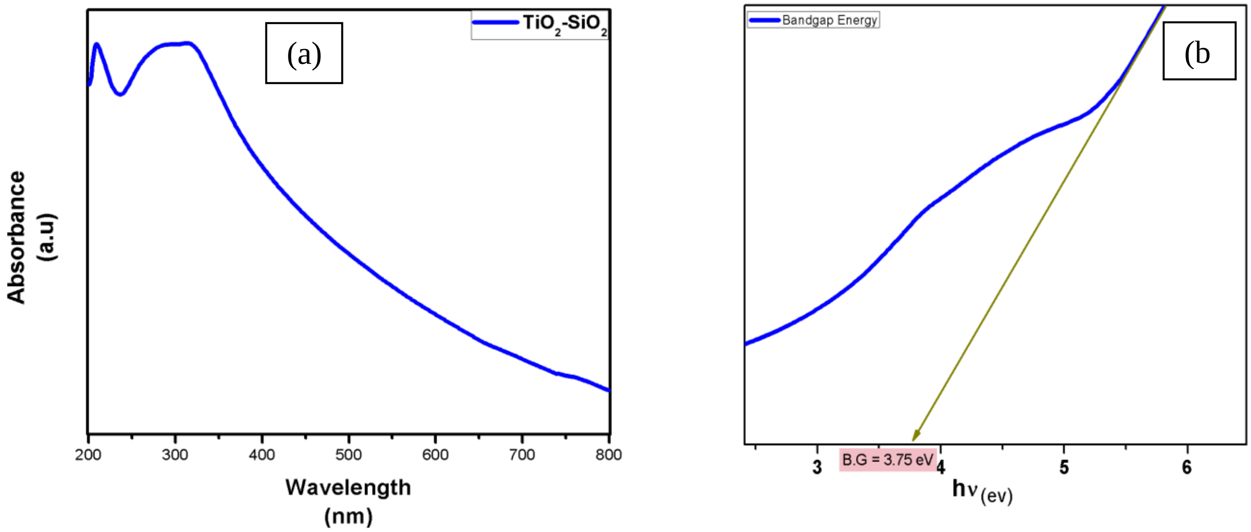


Fig 2: (a) UV-Vis spectra and (b) Band gap energy of TiO_2-SiO_2 nanocomposite.

Fig. 2 (a) represents the UV-Vis spectra of TiO_2-SiO_2 nanocomposite. It can be observed that optical absorption occurs around 316nm. *Tauc* method was used to estimate the band gap energy by extrapolating the slope of $(\alpha h\nu)^2$ versus hν plot as shown in Fig. 2 (b), where α is the absorbance of the sample and hν is the incident energy. It was approximated to be 3.75eV. In general, anatase form of TiO_2 has band gap energy of 3.2eV [22]. This increase in band gap energy of TiO_2-SiO_2 nanocomposite may be due to the change in Ti-Ti bond because of the incorporation of Si. Increase in the band gap of the prepared composite allowed for possible applications like photo luminescence, photocatalytic and optoelectronic device fabrications [23-24].

FTIR spectra analysis of TiO_2–SiO_2 composites before and after photo degradation of dye is represented in Fig 3. It was observed that absorption band at 1047 cm^{-1} is the characteristics peak for Si-O-Si bending vibrations. The broad absorption at 1629.63 cm^{-1} and 3397 cm^{-1} is due to -OH bending vibrations. The peak observed at 927.57 cm^{-1} corresponds to Si-O-Ti vibrations. The band observed at 450-610 cm^{-1} is due to Ti-O stretching [18]. After photo degradation some changes in characteristics peaks has been observed where little shifting and change in absorbance value of 1047 cm^{-1} and 927 cm^{-1} peaks were observed i.e. peaks corresponding to Si-O-Si and Si-O-Ti bond. This shifting is mainly due to the adsorption and degradation of dye and it also indicates that these bonds were involved in adsorption and photo degradation suggesting probable phenomenon of physical adsorption of dye on nanoparticles.

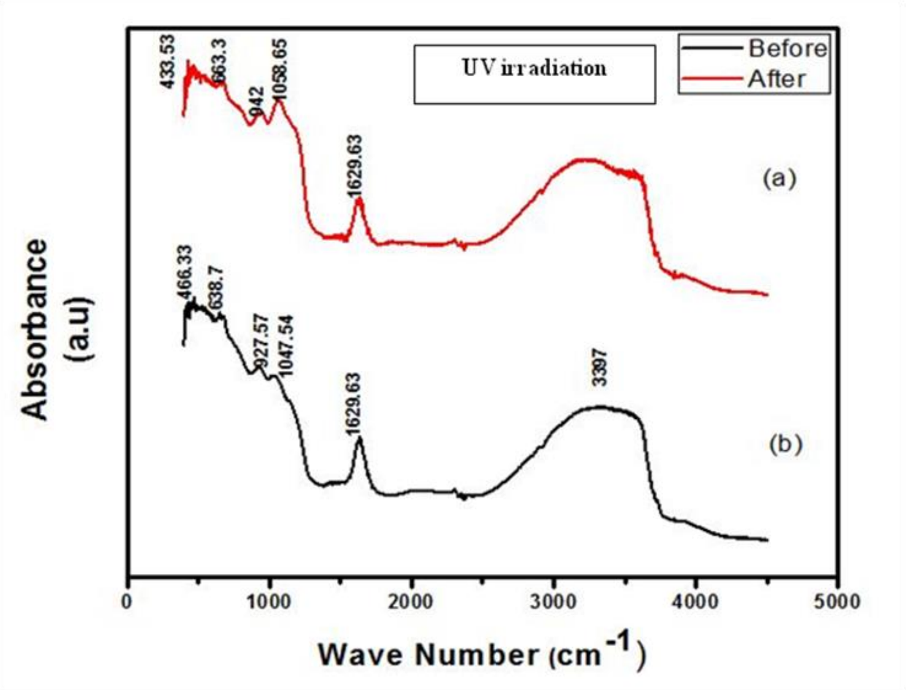


Fig 3: FT-IR spectra of TiO2–SiO2 nanocomposites before and after photo degradation.

Photocatalytic activity and measurement

Selection of the best ratio

Effect of different weight ratios on dye degradation is shown in Fig. 4. The dye sample along with nanocomposite was subjected to 30 min of adsorption in dark followed by 15 min of UV irradiation. It may be observed that when TiO_2: SiO_2 is 60: 40 there is about 74.59% degradation of dye, which increases with increase in ratio of TiO_2

in TiO_2:SiO_2 i. e. attains maximum (99.58%) at TiO_2-SiO_2 of 70:30. But, further increasing the TiO_2 ratio in TiO_2:SiO_2 to 80:20 shows reduction in degradation efficiency to 96.84% and for 90:10 ratio shows 90%. In absence of SiO_2, i. e. for pure TiO_2 dye removal percentage was only 58%.

This variation in dye removal can be explained as; when TiO_2 share is low (60:40 ratio) available sites of TiO_2 is also low in the solution, so the contact of dye with the TiO_2 particles is also low. Dye is degraded mainly due to the photo activity of TiO_2 particles. As less amount of dye reacts with photo generated electron-hole pairs, it results in lesser degradation for 60:40 ratio. When TiO_2:SiO_2 is 70:30 maximum degradation took place due to the reason that, SiO_2 is a very good absorbent and 30 parts of SiO_2 is sufficient enough to adsorb and hold maximum amount of dye on its surface. With 70parts of TiO_2 most of the dye molecules are in contact with TiO_2 particles and when subjected to photo reaction maximum degradation of dye was obtained. Increasing concentration of TiO_2 in 80:20 and 90:10 ratios results in decrease of SiO_2 causing decrease in adsorption of dye and holding on its surface causing less available dye for further photodegradation. In case of pure TiO_2 there was large decrement of dye degradation percentage (58%). This can be explained as TiO_2 is not a good adsorbent although it shows good initial adsorption but with time dye separated out from its surface After 20min adsorption in dark most of the dye was not in contact with TiO_2 particles. Under UV irradiation when electron-hole pairs are generated due to photo activity of TiO_2, they react with fewer amounts of dye molecules which are in contact with TiO_2 particles resulting in less photoactivity. For further evaluation of effect of time on adsorption and UV irradiation three ratios of TiO_2:SiO_2 was selected i.e. 70:30, 80:20, 90:10.

Effect of time on adsorption

Fig.5 shows the adsorption percentages with respect to time for different weight ratios of TiO_2: SiO_2 using 2gm/L dose. From this graph it was observed that both adsorption and desorption of dye on nanocomposite surface was taking place. When TiO_2-SiO_2 nanocomposite was added to dye solution, there exists a difference in surface charge. TiO_2-SiO_2 was negatively charged and methylene blue dye was positively charged. This difference in charge favored the diffusion of dye into the TiO_2-SiO_2 surface. This explains an initial increase in adsorption percentages of dye i.e. up to 20 min.

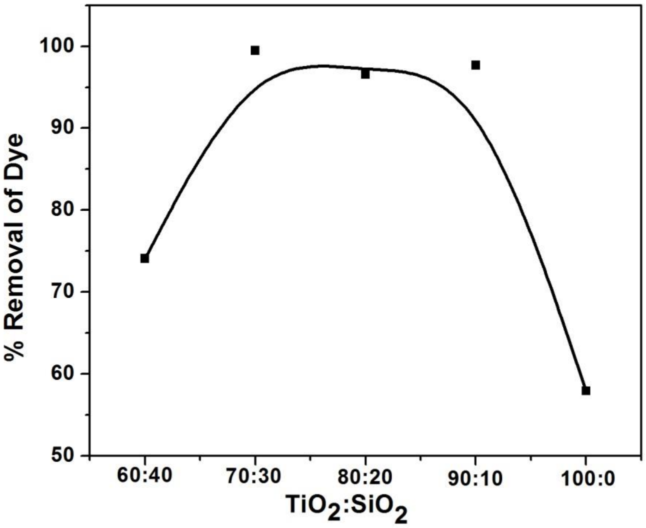


Fig. 4: Effect of different weight ratios of TiO2–SiO2 nanocomposites on dye degradation.

But after certain time i.e. at 30 min, decrease in adsorption percentages or desorption was noticed. This might be due to when all available pores were occupied by dye attaining a state of equilibrium and no pores were available for further adsorption. But the particles are in continuous rotational motion and this rotational motion exerts centrifugal force on it. Because of this force some dye molecule could be separated out from t surface of TiO_2-SiO_2 and raise t concentration of solution. Again, after certa time these dye molecules went to t unoccupied pores and concentration solution decreases or in another wo adsorption happened. Another point that c be made from this observation is there is permanent degradation of dye in da adsorption. It can be concluded that 20m adsorption time is sufficient for maximu possible adsorption. So, from this stud adsorption time of 20 min was selected.

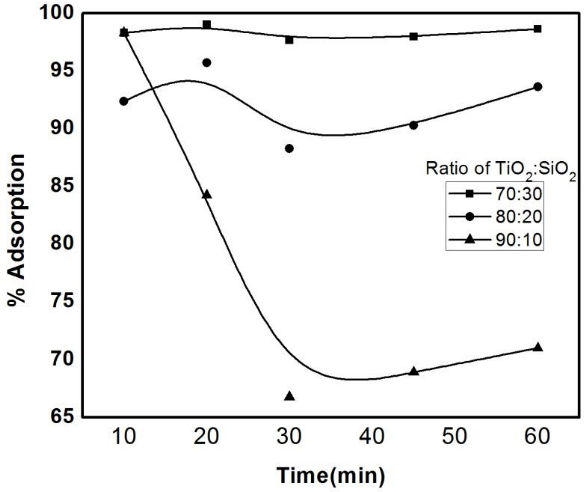


Fig 5. Effect of time on adsorption for different weight ratios of TiO_2–SiO_2 nanocomposites

Effect of UV irradiation time on Dye degradation

Fig. 6 shows the percentage removal of dye degradation with respect to time for three ratios of TiO_2: SiO_2 after dark adsorption with 2g/L dose. In all three ratios with increase in time, percentage in degradation of dye has been observed. Continuous increase in percentage removal indicates that degradation by photocatalysis phenomenon was prevalent under UV irradiation unlike dark adsorption.

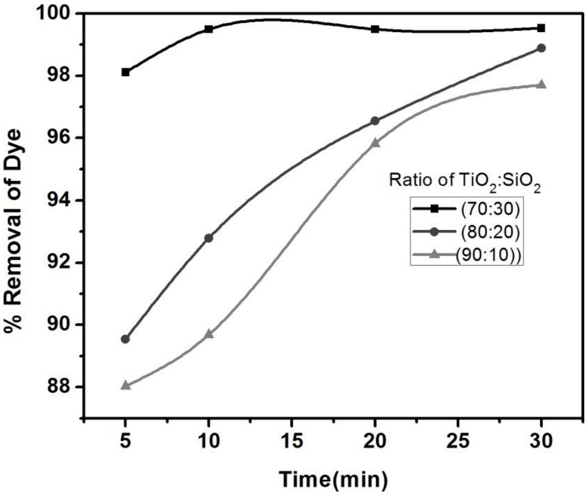


Fig 6. Effect of UV irradiation time on dye degradation for different weight ratios of TiO2–SiO2 nanocomposites.

It was observed that after 10min of UV irradiation there was more than 90 percent decrease of dye concentration. From the above two discussion it can be concluded that 20 min adsorption time is the optimum adsorption time and 10 min UV irradiation is sufficient for about 90% degradation of dye. For further experiments 20 min of adsorption followed by 10min UV irradiation was selected as optimum adsorption and UV irradiation time.

Effect of variation of dose on dye degradation

Fig. 7 shows the effect of different doses (1.5g/L, 2g/L, 2.5g/L) on dye degradation using 70:30 weight ratio of TiO_2: SiO_2 and 30ppm dye solution. From the graph it was observed that, 2g/L dose of nanocomposite shows the highest dye degradation as compared to other two doses. 96.9% degradation was achieved with 1.5g/L and this may be due to the less available photoactive sites as TiO_2 concentration is less.

Interestingly, for 2.5g/L dose dye degradation was 94.82% which might be due to the reason that with increase in catalyst dose, total active surface area increases, hence availability of more active sites on catalyst surface [25]. But, at the same time, turbidity of the suspension increases due to more TiO_2 which will decrease the penetration of UV light by scattering of light and hence effectiveness of catalyst decreases [26]. Also, with increases in dose of catalyst the chances of agglomeration increase [27].

Thus, it might be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering. 2g/L was selected as the optimum dose of nanocomposite.

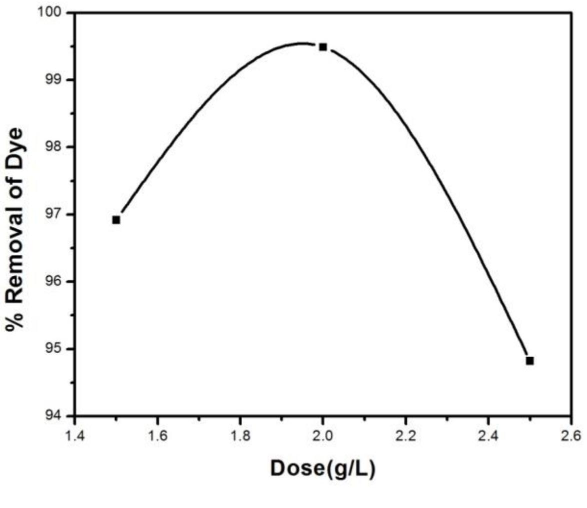


Fig 7. Effect of varying doses of TiO_2–SiO_2 nanocomposites on dye degradation.

Effect of varying dye concentration on dye degradation

Fig. 8 shows the graph of dye removal with respect to dye concentration. For 10ppm dye concentration there was 99.86% removal of dye after 20min dark adsorption and 10min UV irradiation with 2g/L dose. About 99.49% and 94.82% removal was obtained for 30ppm and 50ppm of dye solution respectively. For a fixed amount of irradiation time i.e. 10 min for this study, percentage of dye degradation decrease with increase in dye concentration due to presence of more numbers of dye molecules in the solution.

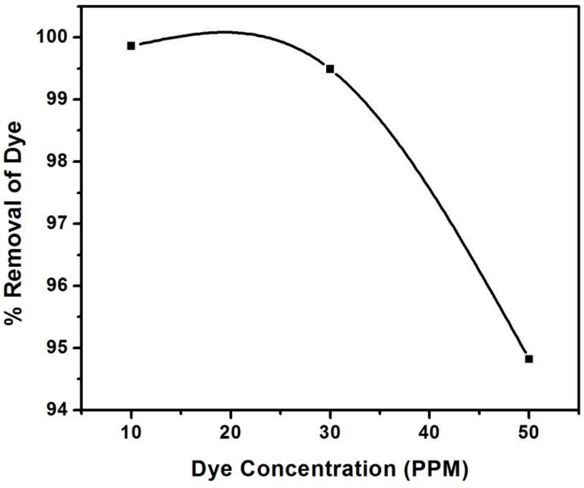


Fig 8. Effect of varying dye concentration on dye degradation.

Conclusion

TiO_2-SiO_2 nanocomposite has been successfully synthesized by simple, low-cost sol-gel technique using HNO_3 as a peptizing agent. The XRD result exhibits that all TiO_2 crystal are in anatase phase and SiO_2 is in amorphous phase. Average crystallite size of this composite calcined at 550ºC was calculated to be lowest i.e. 6.42 nm. This might be due to the reduction in grain growth by Si atom. Surface morphology analysis shows particles are of irregular shape and in agglomerated, dense form. Analysis of FT-IR indicates formation of nanocomposite due to the existence of Si-O-Ti (927.57 cm-1), Si-O-Si (1047 cm-1) and Ti-O (450-610 cm-1) bonds. EDS analysis shows the existence of Ti, Si and O elements suggesting absence any impurities in nanocomposite. UV-VIS spectrum analysis of the nanocomposite depicted little increase in bandgap energy as compared to pure anatase TiO_2 i.e. from 3.2 eV to 3.75eV. This rise might increase the reactivity of photo generated electron, which in turn increases the photo activity of this nanocomposite. In this study it was observed that 70:30 ratio of prepared nanocomposite has the highest photocatalytic activity for degrading 30ppm of MB dye with 2 g/L dose. Optimum adsorption time was found to be 20 min followed by 10 min of UV irradiation. From the above study it might thus be concluded that 2g/L dose of 70:30 ratio (TiO_2: SiO_2) was sufficient for 99.49% photo degradation of 30 ppm dye solution within 30 min (20 min adsorption and 10 min UV radiation). This composite shows better photocatalytic performance than the commercial pure TiO_2 nanoparticles and thus may replace the need of costlier TiO_2 with more cost-effective nanocomposite for industrial application of dye removal. The authors will further utilize the scope of coating the nanoparticles on electrodes for direct use in dye industries.

Acknowledgement

The authors would like to acknowledge Jadavpur University and All India Council for Technical Education for providing funding assistance to carry out the research work.

Conflict of interest

The author declares no conflict of interest.

References

[1] Lee, S.Y. and S.J. Park, 2013. TiO_2 photocatalyst for water treatment applications, Journal of Industrial and Engineering Chemistry, 19 (6): 1761-1769.

[2] Ochiai, T. and A. Fujishima, 2012. Photoelectrochemical properties of TiO_2 photocatalyst and its applications for environmental purification, Journal of Photochemistry and Photobiology A: Chemistry, 13 (4): 247– 262.

[3] Ravirajan, P., S. A. Haque, J. R. Durrant, D. D. C. Bradley and J. Nelson, 2005. The Effect of Polymer Optoelectronic Properties on the Performance of Multilayer Hybrid Polymer/TiO2 Solar Cells, Advanced Functional Materials, 15(4): 609 – 618.

[4] Li, J., Y. Lu, P. Lan, X. Zhang, W. Xu, R. Tan,W. Song and K.L. Choy, 2013. Design, preparation, and durability of TiO2/SiO2 and ZrO2/SiO2 double-layer antireflective coatings in crystalline silicon solar modules, Solar Energy. 89: 134–142.

[5] Euvananont, C., C. Junin, K. Inpor, P. Limthongkul and C. Thanachayanont, 2008. TiO_2 optical coating layers for self-cleaning applications, Ceramic International, 34 (4): 1067–1071.

[6] Yu, Y., M.Z. Zhang, J. Chen, and Y.D. Zhao, 2013. Homogeneous synthesis of SiO2/TiO2 nanocomposites with controllable shell thickness and their enhanced photocatalytic activity, Dalton Transactions, 42 (4) 885–889.

[7] Lv, K., B. Cheng, J. Yu, and G. Liu, 2012. Fluorine ions-mediated morphology control of anatase TiO2 with enhanced photocatalytic activity, Physical Chemistry Chemical Physics, 14 (2012) 5349–5362.

[8] Chen, X. and S.S. Mao, 2007. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications, Chemical Reviews, 107 (7): 2891−2959.

[9] Saravi, H.I., Z. Mehdi, K. Ahmad and D. Patrick, 2016. Synthesis, characterization, and photocatalytic activity of TiO2–SiO2 nanocomposites, Desalination and Water Treatment, 57 (31): 14647-14655.

[10] Heba, G., E.S. Radwa, M. Dalia, M. Marwa, M. Yasser and G. Tahani, 2014. Use of SiO2 - TiO2 Nanocomposite as Photocatalyst for the Removal of Trichlorophenol: A Kinetic Study and Numerical Evaluation, Chemistry and Materials Research. 6 (6): 63-81.

[11] Yu, J.C., J. Yu and J. Zhao, 2002. Enhanced photocatalytic activity of mesoporous and ordinary TiO2 thin films by sulfuric acid treatment, Applied Catalysis B: Environmental, 36 (1): 31–43.

[12] Zhu Y., L. Zhang., W., Yao, and L. Cao, 2000. The chemical states and properties of doped TiO2 film photocatalyst prepared using the Sol–Gel method with TiCl4 as a precursor, Applied Surface Science, 158 (1): 32–37.

[13] Liu, C., D. Yang, Y. Jiao, Y.Tian, Y. Wang, and Z. Jiang, 2013. Biomimetic Synthesis of TiO2−SiO2−Ag Nanocomposites with Enhanced Visible-Light Photocatalytic Activity, ACS Appl Mater Interfaces. 5 (9): 3824−3832.

[14] Sharma, A.K. and B.K. Lee, 2020. Surfactant-aided sol-gel synthesis of TiO2–MgO nanocomposite and their photocatalytic azo dye degradation activity, Journal of Composite Materials. 54 (12): 1561-1570.

[15] Wei, J., J.C. Zhang, 2017. Fe_2O_3/TiO_2 nanocomposite photocatalyst prepared by supercritical fluid combination technique and its application in degradation of acrylic acid, In the Proceedings of 2017 IOP Conference Series: Materials Science and Engineering, pp.19-21.

[16] Yan, N., Z. Zhu, J. Zhang, Z. Zhao and Q. Liu, 2012. Preparation and properties of ce-doped TiO2 photocatalyst, Material Research Bulletin, 47 (8): 1869–1873.

[17] Balachandran, K., R. Venckatesh, R. Sivaraj and P. Rajiv, 2014. TiO2 nanoparticles versus TiO2–SiO2 nanocomposites: A comparative study of photo catalysis on acid red 88, Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy, 128: 468–474.

[18] Yu, H.F. and S.M. Wang, 2000. Effects of water content and pH on gel-derived TiO_2–SiO_2, Non-Crystalline Solids. 261: 260–267.

[19] Dung Dang, T.M., D. Dam Le, V. Thang Chau and M. Chien Dang, 2010. Visible-light photocatalytic activity of N/SiO2–TiO2 thin films on glass, Advances in Natural Sciences: Nanoscience and Nanotechnology, 1 (1): 1-5.

[20] Dette, C., M.A. Pérez-Osorio, C. S. Kley, P. Punke., C.E, Patrick., P. Jacobson., F. Giustino., S. Jung Jung and K. Kern, 2014. TiO2 Anatase with a Bandgap in the Visible Region, Nano Letters, 14 (11): 6533−6538.

[21] Khanna, P.K., N. Singh and S. Charan, 2007. Synthesis of nano-particles of anatase-TiO2 and preparation of its optically transparent film in PVA, Mateiarls Letters, 61 (25): 4725–4730.

[22] Xiaoming, F., 2015. Synthesis and Optical Absorpition Properties of Anatase TiO_2 Nanoparticles via a Hydrothermal Hydrolysis Method, Rare Metal Materials and Engineering, 44 (5): 1067- 1070.

[23] Chen, J. P. and S. Wu, 2004. Acid/Base-Treated Activated Carbons: Characterization of Functional Groups and Metal Adsorptive Properties, Langmuir. 20 (6): 2233-2242.

[24] Kansal, S.K., N. Kaur and S. Singh, 2009. Photocatalytic Degradation of Two Commercial Reactive Dyes in Aqueous Phase Using Nanophotocatalysts, Nanoscale Reserach Letters, 2009; 4(7): 709–716.

[25] Gonclaves, M.S.T., A.M.F. Oliveira-Campose, E.M.M.S. Pinto, P.M.S. Plasencia and M.J.R.P Queiroz, 1999. Photochemical Treatment of Solutions of Azo Dyes Containing TiO2, Chemosphere, 39:781-786.

[26] Daneshvar, N., D. Salari and A.R. Khataee, 2003. Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters, Journal of Photochemistry and Photobiology A: Chemistry, 157 (1) 111–116.