Synthesis of Titania-Silica Nanocomposite for Enhanced Photodegradation of Methylene Blue and Methyl Orange Dyes under UV and Mercury Lights

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Abstract

A special sol-gel method is used to successfully synthesize spherical TiO$_2$/SiO$_2$ nanoparticles from titanium tetra-isopropoxide and tetraethoxysilane precursors. The prepared samples were dried at 110 °C and calcined at 300 °C, 500 °C, and 800 °C. The formed titanium oxide is in a tetragonal structure with significant pure anatase and rutile phase. The estimated particle size of the spherical nanostructure was ~18.40 nm through transmission electron microscopy (TEM) and showed a larger Brunauer Emmett Teller (BET) surface area of 310 m$^2$/gm for the sample calcined at 300 °C. The TiO$_2$ cores are enclosed within SiO$_2$ particles with an average crystallite size of 10-20 nm. In atomic force microscopy (AFM) images, the same sample displayed a well-structured and macro-pore-free morphology. Fourier transform infrared spectroscopy (FT-IR) confirmed the presence of Ti-O-Ti, Si-O-Si, and Ti-O-Si metal oxide bonds to raise the anatase structure of TiO$_2$. The ultraviolet-visible spectroscopy (UV-Vis) of as-synthesized samples reveals the visible absorption region. Photoluminescence spectroscopy (PL) shows a decrease in emission intensity and the emission band splits into sharp peaks to signify the decrease in recombination rate. These properties predict the materials to photo-degrade organic dyes. The material's photocatalytic activity was evaluated for degradation of methylene blue and methyl orange dyes. It is found that the sample calcined at 300 °C exhibits a better photodegradation for methylene blue (MB, 80-85%) than methyl orange (MO, 70-75%) under mercury light within 2 hours.

Keywords: TiO$_2$/SiO$_2$ nanocomposite; photo-degradation; methylene blue (MB); methyl orange (MO).

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1. Introduction

Titanium dioxide (TiO$_2$) has been of great interest to materials scientists and physicists due to its unique properties, and it has been widely used for a variety of technological applications such as photocatalysts,[12] solar cells, sensors,[13-15] and memory devices. Due to its large surface area, titanium nanopowder in most studies is used. Most studies in the last few decades have concentrated mainly on suspending TiO$_2$ powder as compared to the good photocatalytic activity of thin film.[8]

The sol-gel process has many advantages, including being environmentally friendly, having a low processing temperature, better homogeneity, high purity, precise composition control, and being cost-effective.[4,7] TiO$_2$ is a typical n-type semiconductor with three crystal morphs in nature: anatase, brookite, and rutile. Brookite is the rare phase, and rutile is a high-temperature stable phase, whereas anatase is not as thermodynamically stable as rutile. Basically, both anatase and rutile have a tetragonal crystal structure.[7,10] The SnO$_2$/TiO$_2$ and SiO$_2$/TiO$_2$ mixed oxides have been studied with different concentration rates and preparation methods to produce a simple form of single and multi-component oxide in the crystalline or amorphous form.[11,12] N. Venkatachalamp et al. synthesized several crystalline forms of nano TiO$_2$ via the sol-gel method using titanium tetra-isopropoxide as a precursor.[13] The simple sol-gel method was used to
effectively synthesize crystalline TiO$_2$ nanoparticles, which showed the regular rice-grain shape and defined nano-surface as well as large surface area and subsequently higher photocatalytic activity.$^{[14]}$

The mixed oxides such as ZrO$_2$/TiO$_2$, SnO$_2$/TiO$_2$, and SiO$_2$/TiO$_2$ have been studied using various dose rates. Various preparation methods have been investigated, with the sol-gel process being utilized to produce crystalline or amorphous forms of single and multi-component oxides.$^{[15,16]}$ Recent investigations show that TiO$_2$/SiO$_2$ composites give the best support because they integrate both the mechanical and chemical characteristics of active titania. Kimura Isao et al. claimed that a simple technique may be used to make a composite microsphere and TTIP (titanium (IV) isopropoxide) had a significant effect on the morphology of titania/silica composite microspheres produced using sol-gel in reverse suspension.$^{[17]}$ SiO$_2$, which has strong thermal stability and carrier characteristics, is commonly employed in organic compounds to increase active sites on TiO$_2$ particles, which improves photocatalytic activity.$^{[18,19]}$ Recently, the synthesized TiO$_2$/SiO$_2$ composite nanoparticle by sol-gel method served as an important item in controlling the surface properties, to provide distinct benefits in the production of highly dispersed tetrahedral coordinated materials.$^{[20]}$ The photocatalytic activity of TiO$_2$ can be improved by the addition of SiO$_2$, which increases the surface area and surface acidity and enhances the thermal stability of the phase of TiO$_2$ particles of the catalysts, allowing an increase in the adsorption of pollutant molecules.$^{[21,22]}$

In this work, we report a simple and environment-friendly sol-gel method to synthesize TiO$_2$/SiO$_2$ nanocomposite. The characterization of the nanocomposite to determine morphologies were done by scanning electron microscopy (SEM), atomic force microscopy (AFM), and BET for surface area, X-ray diffraction (XRD) for phase identification and crystallite size. The functional group and various bonding to confirm the formation was done by Fourier-transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM). Their optical behavior was studied by absorption spectra using UV-visible spectroscopy and emission spectra through photoluminescence spectroscopy (PL). Photocatalytic activities of these synthesized nanocomposites were studied by methylene blue (MB) and methyl orange (MO) dyes under UV and Mercury light sources.

### 2. Experimental details

#### 2.1. Materials

All of the chemicals used in the study were analytical grade purity with no further purification. De-ionized water was used to make all of the solutions. Tetraethoxysilane (TEOS) (99.9%, Sigma Aldrich) was used as a SiO$_2$ precursor and titanium tetra-isopropoxide (TTIP) (99.9%, Sigma Aldrich) was used as a TiO$_2$ precursor. Along with ethanol (99.9%, Merck), the catalyst was hydrochloric-acid (HCl) (99.9%, Merck).

#### 2.2 Synthesis of the TiO$_2$/SiO$_2$ nanocomposite

At 60 ºC, the synthesis was carried out with constant stirring. An electromagnetic stirring of 1100 rpm was used to stir the mixture. 1 mole of titanium tetra-isopropoxide (TTIP) was prepared for 10 minutes with ethanol dissolving and deionized water (35 ml) was stirred, at a pH of 2.5. Then 1 mole of hydrochloric acid (HCl) was added to the aforementioned mixture and agitated for 50 minutes. A yellowish homogeneous transparent solution was achieved at a pH of 1. One mole of tetraethoxysilane (TEOS) was slowly added to the above solution, the mixture was mixed. It resulted in the formation of a white precipitate. Filtration was used to collect the precipitate, which was then washed with deionized water. Then, it was dried at 110 ºC in an oven for 2 hours, the crystalline product was ground to form a fine white powder. The powder was finally split into three equal parts, one of which was calcined for one hour at 300 ºC, and the third at 800 ºC to eliminate water and solvent before cooling naturally. The calcination was done in a programmed furnace. To enhance material characterization and execute a photocatalytic test, composite powder TiO$_2$/SiO$_2$ was produced. Fig. 1 depicts a schematic flowchart of the TiO$_2$/SiO$_2$ synthesized samples process using a TTIP precursor for TiO$_2$ and a TEOS precursor for SiO$_2$, respectively.

![Fig. 1 A flow diagram to represent the sol-gel process for the synthesis of TiO$_2$/SiO$_2$ nanocomposites.](image-url)
2.3 Characterizations of the synthesized TiO$_2$/SiO$_2$ nanocomposite
The prepared TiO$_2$/SiO$_2$ nanocomposites were characterized for their optical properties using UV-visible spectroscopy recorded with an HR4000 High-Resolution Miniature Fiber Optics Spectrometer having an optical resolution as well as 0.025 nm (FWHM). The photoluminescence spectra were obtained using a Hitachi F-7000 fluorescence spectrophotometer. Surface morphology was studied by using SEM (JEOL-JSM-6390). The TEM micrographs were recorded using a JEM 200CX transmission electron microscope (JEOL, Tokyo, Japan) with a 120 kV accelerating voltage. The NT-MDT Solver Next, Software-Nova PX was used for the samples to conduct AFM studies. The samples were placed on a clean glass plate. The Bruker D8 Advance X-ray diffractometer was used to measure the X-ray diffraction patterns of samples. A sealed tube was used to generate an X-ray with a wavelength of 0.154 nm (Cu-K$_α$). X-rays were detected using a rapid counting detector based on Silicon strip technology (Bruker Lynx Eye detector). These X-ray diffraction patterns were used to identify phases and estimate the size of an average crystallite. Debye Scherrer’s formula was used to calculate the crystal size. The FT-IR spectra were measured using a Bruker Model-Vertex 70 Spectrometer in the spectral range of 1000 to 4000 cm$^{-1}$. Quantachrome – Autosorb – BET surface area analyzer was used to determine the BET surface area of prepared catalysts. To investigate the photocatalysis efficiency of all produced samples, the UV–vis absorption spectra and photoluminescence (PL) emission spectra were used.

2.4 Photocatalytic activity of the synthesized TiO$_2$/SiO$_2$ nanocomposite
The synthesized catalyst photocatalytic activity was characterized by experiments with ultraviolet irradiation and MB and MO dyes were used as a model compound for visible irradiation. To test the photocatalytic activity, a visible mercury lamp of 50 W and a UV Xenon lamp of 125 W is used. Photocatalysis experiments were performed using a self-designed photo-degradation reactor box and 100 mL glass beaker. In order to prevent light from entering the sources, the side wall beaker was covered by aluminum foil. UV and visible light sources on the reactor top were fitted for uniform lighting to illuminate the sample. The distance between the lamp and the photocatalytic device was approximately 1 cm. All the experiments were carried out in a dark room with no other light sources present. The setup used for the photodegradation experiment is shown in Fig. 2. Water based solution of 1×10$^{-4}$ m/L MB and MO was prepared. A 0.05 gm powder catalyst suspension was added to a 100 mL aqueous solution of MB or MO. The mixture was mixed in a glass beaker and stirred for 30 minutes in dark, which allowed adsorption and even uniform dispersion using a UV or visible light source. The experiment was conducted under illuminated light at room temperature and 1-2 pH. After 30 minutes of illumination, a 5 mL solution was collected and centrifuged to remove catalyst residues. This solution was then used for UV-vis spectrometer analysis. After every 30 minutes of interval, a 5 mL solution of 664 nm and 332 nm of the corresponding maximum absorption wavelength ($λ_{\text{max}}$) in MB and MO was taken from the beaker, centrifuged, and analyzed through a UV-vis spectrometer.

The concentration of remnant dye is the measure of the amount present in that solution. UV-Vis spectroscope technique was used to determine this amount. A first-order equation describes the dye degradation in an aqueous solution as shown in Equation (1):$^{[23]}$

$$C_t = C_0 e^{-kt} \quad \text{(1)}$$

The percentage of dye degradation was calculated by Equation (2):

$$\text{Degradation} \% = \left[1 - \frac{C_t}{C_0}\right] \times 100 \quad \text{(2)}$$

where $C_0$ represents the dye concentrations in the solution prior to exposure and $C_t$ represents the dye concentrations in the solution after exposure, $t$ represents the time period of exposure, and $k$ represents the rate of degradation response. $C_0$ and $C_t$ are proportional to the intensity of the particular dye’s absorption peak.

![Fig. 2 Schematic of photocatalytic degradation setup.](image)

3. Results and discussion
3.1 Characterizations and properties of synthesized TiO$_2$/SiO$_2$ nanocomposites
SEM characterization was used to study the morphology of the synthesized TiO$_2$/SiO$_2$ nanocomposites. The average particle size of the TiO$_2$/SiO$_2$ composite sample is within the nanometer range as shown by SEM images, Fig. 3. From Fig. 3(a), it is observed that the as-synthesized TiO$_2$/SiO$_2$ nanocomposite sample calcined at 300 °C temperature have spherical nanoparticles with uniformly well-defined boundaries. In calcination at 500 °C, the nanoparticle is spherical in shape but boundaries are diffused as shown, in Fig. 3(b). On calcined at 800 °C, the nanoparticle consists of many uniform pores, which are aggregated as shown in Fig. 3(c). According to the SEM photographs of the prepared sample,
the agglomeration takes place during the crystal growth with increasing calcination temperature. In the results, it can be concluded that the samples calcined at 300 °C show well-defined boundaries with no agglomeration. This confirms the particle size by means of TEM and surface morphology by AFM. The AFM has been used to characterize the surface morphology of the prepared sample. The powder sample was mixed in acetone and then sonicated for up to 30 min for AFM characterization. The solution was then spin-coated on the thin glass support by Holmarc’s spin coater (model no: HO-TH-05) at 6000 rpm. The structure of nanoparticles was identified through AFM images in 5μm × 5μm area.

The well-structured morphology has been displayed in AFM images of the TiO$_2$/SiO$_2$ composite, which has a macro-pore-free and uniform morphology calcined at 300 °C as shown in Fig. 4 (in 2D image). From Fig. 4, the 3D topography images give details about the surface roughness up to 2.169 nm. When TiO$_2$/SiO$_2$ is calcined at 300 °C, the root means square roughness is thus reduced and the thin film becomes relatively smooth and has no agglomeration in the sample. In the study, the surface area was calculated using BET, total pore volume, and average pore diameter for each material. The average pore diameter is 62.49 Å for synthesized TiO$_2$/SiO$_2$ samples calcined at 300 °C and the total pore volume is 0.410 cc/gm with a specific surface area is 310 m$^2$/gm. Subsequently, the result showed that the TiO$_2$/SiO$_2$ sample calcined at 300 °C has a higher specific surface area, indicating that the material prepared in the presence of SiO$_2$ was more thermally stable. The TiO$_2$/SiO$_2$ sample calcined at 300 °C has effectively improved the specific surface area of the solid samples, because of its high crystallinity and suppressed particle growth, and reduced pore diameter (as determined by SEM, TEM, and XRD studies) to improve the photocatalytic activity.

XRD analysis has been done to detect the TiO$_2$/SiO$_2$ nanocomposite phase composition. X-ray diffraction patterns of TiO$_2$/SiO$_2$ nanocomposite powder samples are displayed in Fig. 5. As seen below, the Scherrer equation determined the average crystallite size of the sample. Scherrer’s equation is illustrated as Equation (3)

$$D = \frac{K \lambda}{\beta \cos \theta}$$  \hspace{0.5cm} (3)

The calculation of the crystallite size (D) from broadening of the key peak (101) anatase peak is done by Equation (3), where $K$ is a constant depending on the crystallite shape (0.9), $\lambda$ is X-ray wavelength (in this case, $\lambda = 1.5418$ Å for Cu-Kα radiation), $\beta$ is the full width at half maxima (FWHM) of the diffraction peaks and $\theta$ is the Bragg’s angle, and also the unit
Fig. 5 Powder XRD pattern of as-synthesized TiO$_2$/SiO$_2$ nanocomposite calcined at a. 300 °C and b. 800 °C temperatures (A-anatase and R-rutile).

cell volume as correlated to the reference pattern. On comparing our XRD result from the JCPDS Card No. 850335 for SiO$_2$, JCPDS Card No. 21-1272 for TiO$_2$ of the anatase phase, and JCPDS Card No. 21-1276 for TiO$_2$ of rutile phase.

In the diffraction pattern, no clear peaks for SiO$_2$ nanoparticles are observed because of their amorphous nature. The diffractogram shows the strongest TiO$_2$ diffraction peaks in the anatase phase. The peaks of anatase TiO$_2$ appeared at 2θ=25.3° (101), 37.8° (004), 48.0° (200), 53.9° (105), 62.7° (204), 68.8° (116) and 75.0° (215). In XRD results, it can be clearly observed that the synthesized material has a tetragonal crystal structure with the lattice parameters: a= 3.785 Å and c= 9.513 Å. From Fig. 5(a), the TiO$_2$/SiO$_2$ nanocomposite calcined at 300 °C, and the anatase peaks are presented, indicating a high-quality crystalline material. However, the results show that the particles with regular shapes and smaller particle sizes are pronounced. At 300 °C, the average crystallite size of the TiO$_2$/SiO$_2$ composite nanoparticle was 6.40 nm and the observed changes within the unit cell volume of the TiO$_2$/SiO$_2$ composite are 135.48 Å$^3$.

On increasing the calcination temperature up to 800 °C, TiO$_2$ powder transforms in the rutile phase confirmed by the diffraction peaks seen in Fig. 5(b). Rutile TiO$_2$ appeared at 2θ=27.4° (110), 36.0° (101), 39.1° (200), 54.3° (211), 56.6° (220), 64.5° (310), 69.2° (301), 70.3° (112). Results from XRD analysis have shown that the synthesized material has a tetragonal crystal structure and has a primitive lattice with lattice parameters: a=4.5933 Å and c=2.9592 Å. The average crystallite size of the 800 °C temperature sample TiO$_2$/SiO$_2$ nanocomposite was 21.42 nm, and a change in the TiO$_2$ unit cell volume was 62.72 Å$^3$. This indicates that the rutile nuclei tend to grow more than the anatase, and shows that with increasing the calcination temperature, the crystallite size increases. However, the intensity of the diffraction peaks ii increased as the calcination temperature is raised, which indicates an improvement in the material crystallinity. This result indicates that the TiO$_2$/SiO$_2$ nanocomposite calcined at 300 °C could effectively retard the growth of nanoparticles, clear crystallinity, and reduce the crystallite size.

FT-IR analysis was performed with KBr and fine powder mixed in order to identify the component composition and functional groups of unknown samples. FT-IR is a tool like the fingerprint of all organic compounds and some inorganic compounds, which cannot be the same for 2 different samples. FT-IR spectra were taken at room temperature within the spectral range between 600 to 4000 cm$^{-1}$. The FT-IR spectrum of the TiO$_2$/SiO$_2$ nanocomposite sample is shown in Fig. 6. In the sample calcined at 300 °C, the peaks at 3444 cm$^{-1}$- 3182 cm$^{-1}$ and 1631 cm$^{-1}$ show the bending vibration of -OH. In the spectrum of TiO$_2$, the peak at 671 cm$^{-1}$ shows the stretching vibration of Ti-O and the peak at 1458 cm$^{-1}$ shows the stretching vibrations of Ti-O-Ti.

The observed band at around 1219 cm$^{-1}$-1178 cm$^{-1}$ can be assigned to the stretching and bending of the Si-O-Si bond. The strong bands at 1060 cm$^{-1}$ are a duo to the stretching of Si-OH and Ti-OH. The sample shows another weak band at around 950 cm$^{-1}$. The Si-O species of Si-O-Ti or Si-O defect sites that are formed due to the inclusion of Ti$^{4+}$ ions into SiO$_2$ matrixes in four-fold coordination with SiO$_4^{4-}$ oxygen has been designed for stretching this band. The absorption peak at 766 cm$^{-1}$ shows the bending vibrations of Ti-O-Si. On calcination, the TiO$_2$/SiO$_2$ sample at 300 °C, other absorption bands are hindered. This result of FT-IR indicates that the stable TiO$_2$/SiO$_2$ composite nanoparticles were prepared by TiO$_2$ with SiO$_2$ nanoparticles and confirmed that the metal oxide bond of pure TiO$_2$/SiO$_2$ solid solution is present to give rise to anatase structure and suppresses the transformation from anatase to rutile of TiO$_2$ and enhances the crystallinity in SiO$_2$.\[24\]
Fig. 6 FT-IR absorption spectra of TiO$_2$/SiO$_2$ nanocomposite calcined at 300 °C temperature.

The TEM was used to analyze the estimated particle size of the prepared samples of TiO$_2$/SiO$_2$ calcined at 300 °C. The TEM micrographs in Fig. 7 show nearly spherical particles, which are highly uniformly dispersed and less aggregated. The mean particle sizes measured are 18.40 nm. The main noticeable result is that the TiO$_2$ particles are surrounded by SiO$_2$ spheres of around 10-20 nm in size. This structure plays an essential role in the design and use of these highly efficient photocatalytic systems. The formation of the Ti-O-Si on the interface is also confirmed by FT-IR spectra by a visible peak at around 950 cm$^{-1}$.

Fig. 7 TEM micrograph of TiO$_2$/SiO$_2$ nanocomposite calcined at 300 °C. The core structure of TiO$_2$ covered with particles of SiO$_2$.

UV-Visible characterization is done for observing the optical behavior of the synthesized material. The UV-visible absorption spectra of the TiO$_2$/SiO$_2$ nanocomposite synthesized via the sol-gel route calcined at different temperatures are shown in Fig. 8. The band gap energy ($E_g$) was determined by Equation (4).\(^{(36)}\)

$$E_g = \frac{1239.8}{\lambda}$$  \hspace{1cm} (4)

where $E_g$ is the band gap and $\lambda$ is the absorption edge of the spectrum.

Fig. 8 UV-Vis absorption spectra of TiO$_2$/SiO$_2$ nanocomposite calcined at (a) 300 °C, (b) 500 °C and (c) 800 °C.

Fig. 8(a) shows that due to fine particles with a purity anatase phase display high nanoscale crystallinity in the substance. The absorption spectra of TiO$_2$/SiO$_2$ nanocomposite calcined at 300 °C can be attributed to a wavelength of 435 nm as the band gap is 2.85 eV due to the presence of fine particle with pure anatase phase to show a high nano-crystallinity in the
material. From Figs. 8(b and c), the synthesized nanocomposite sample calcined at 500 °C and 800 °C, the absorption peaks, defined at 485.07 nm and 560.00 nm, respectively, show a red shift in the samples.

The band gap of the TiO$_2$/SiO$_2$ composite sample calcined at 500 °C and 800 °C is 2.55 eV and 2.21 (eV), respectively. On calcination at 500 °C and 800 °C, it shows good absorption in the visible region but an aggregation in the material (by SEM analysis). These UV-Vis absorption edges are similar, indicating good absorption in the visible region.

The photoluminescence (PL) spectra of TiO$_2$/SiO$_2$ nanocomposite samples calcined at various temperatures were measured as shown in Fig. 9. This range of emission (270 to 700 nm), which is excited by a particular wavelength gives certain wavelength peaks. The luminescence characteristics depend also on other crucial factors, including solvent, atmosphere materials from the start, etc. [23] From Fig. 9(a), TiO$_2$/SiO$_2$ nanocomposite sample with more crystalline materials show a pure anatase phase calcined at 300°C. The intensity of the PL spectrum is divided into sharp peaks. The result indicated that the formation of resolved multiple lines means that the structure of the positive ion in the spherical structure of TiO$_2$/SiO$_2$ was placed on the well-defined lattice site. Fig. 9(b and c) shows that the emission intensities with a large due to agglomerated lattice sites are calcined with TiO$_2$/SiO$_2$ samples at 500 °C and at 800 °C. Emission peaks at 308.6 nm, 587 nm, and 614.6 nm are shown in the PL sample spectra, TiO$_2$/SiO$_2$ at 300 °C, TiO$_2$/SiO$_2$ at 500 °C, and TiO$_2$/SiO$_2$ at 800 °C. The peak shift towards the red wavelength may suggest that the particle size has grown. The lower PL intensity of PL shows that the rate of recombination decreases and therefore the higher photocatalytic activity decreases. [24] The PL spectra of nanocomposite TiO$_2$/SiO$_2$ calcined with sharp peaks and lower intensity at 300 °C indicates that a decrease in recombination rate is expected, which results in higher photocatalytic activity.

3.2 Photocatalytic properties of synthesized TiO$_2$/SiO$_2$ nanocomposite

Methylene blue (MB) and methyl orange (MO) were photodegraded using visible light and UV light irradiation, respectively. The photodegradation performance of TiO$_2$/SiO$_2$ nanocomposite samples produced and calcined at different temperatures for 120 minutes is shown in Fig. 10 and Fig. 11, respectively. After every 30 minutes up to 2 hours, the concentration of dye was measured based on their characteristic peak in the UV-vis spectra, and the degradation % was calculated using Equation (2). We plotted the degradation% with respect to time for both dyes.

![Fig. 9 Photoluminescence emission spectra of TiO$_2$/SiO$_2$ nanocomposite calcined at (a) 300 °C, (b) 500 °C and (c) 800 °C.](image-url)
Figure 10 and Fig. 11 show that the sample TiO$_2$/SiO$_2$ calcined at 300 °C shows a higher activity in photodegradation because of its small crystallite size and high surface-to-volume ratio. The anatase phase of TiO$_2$/SiO$_2$ exhibits a smaller particle growth with a regular and homogeneous spherical shape, which is beneficial to the photodegradation rate. SiO$_2$ particles effectively inhibit the particle growth in the crystalline TiO$_2$ network, resulting in a more regular and uniform spherical in nature and a faster rate of degradation. TiO$_2$/SiO$_2$ exhibits a higher percentage of photodegradation due to a complete crystallization with anatase phase and smaller particle size and high specific surface area at 300 °C, which were confirmed by TEM, XRD, and BET analysis.[29,31]

However, with the increase of calcination temperatures at 500 °C and 800 °C, with pure rutile phase (from XRD data) with larger crystallite size, particle growth, and sintering rate, the photodegradation activity of three TiO$_2$/SiO$_2$ samples is clearly declined. The calcination sample of 300 °C has a higher photodegradation percentage in comparison with the catalytic performance of all three samples calcined at different temperatures due to complete crystallization with the smaller particle size and larger specific surface area. This is consistent with the fact that anatase, due to its high crystallinity, is more photocatalytically active than rutile.

The results show that, from Fig. 10 and Fig. 11, the photodegradation of MB and MO by TiO$_2$/SiO$_2$ sample calcined at different temperatures shows higher photodegradation performances under visible sources than UV sources. From Fig. 10, TiO$_2$/SiO$_2$ nanocomposite samples calcined at 300 °C show good photodegradation activity of MB under visible light. The degradation of dye by this sample is 90% in visible light and 80% in UV light. This is in good agreement with the results obtained from UV-vis absorption spectra and PL spectroscopy. Photodegradation of MO by TiO$_2$/SiO$_2$ sample calcined at 300 °C displays a greater degradation under the visible irradiation as shown in Fig. 11.

The degradation of this sample is 75% in visible light and 70% in UV light. From Fig. 12, one can see that the TiO$_2$/SiO$_2$ catalyst absorbs the solute more efficiently under visible irradiation, resulting in a significant increase in the rate of photocatalytic breakdown of MB. In the visible region, the sample TiO$_2$/SiO$_2$ has a considerably wider spectrum, increasing the odds of light of the right wavelength striking the photocatalyst surface and activating it.[32] Due to the lower absorption of the dye wavelength, the MB dye performs somewhat better than the MO dye in photodegradation when compared to the photodegradation performance of both dyes in all TiO$_2$/SiO$_2$ samples. The photodegradation of the TiO$_2$/SiO$_2$ catalyst continues to increase with continued irradiation, and no saturation is observed in the overall experiment.[33,34]
The degradation performance of TiO$_2$/SiO$_2$ samples calcined at 300 °C has a slightly higher percentage for MB than MO. The result reveals that the photodegradation performance of TiO$_2$/SiO$_2$ calcined at 300 °C is better due to the large specific surface area, smaller particle size, anatase phase, and high crystallinity.$[15,36]$ The result indicated the best photodegradation performance of MB under the visible light source of a sample with TiO$_2$/SiO$_2$ calcined at 300 °C. Fig. 13 explains well the photodegradation mechanism of dye MB and MO through TiO$_2$/SiO$_2$ nanocomposite under sunlight.

4. Conclusions
The TiO$_2$/SiO$_2$ nanocomposite was successfully synthesized via a sol-gel method. The characterization analyses confirmed the successful synthesis of TiO$_2$/SiO$_2$ nanocomposite. The TiO$_2$/SiO$_2$ calcined at 300 °C has a spherical shape. At higher calcination temperatures, the samples show agglomeration with a large particle size distribution. TiO$_2$/SiO$_2$ composite sample calcined at 300°C displayed a well-structured morphology with a macro-pore-free and uniform site. The XRD patterns consist of several strong diffraction peaks of TiO$_2$ in the tetragonal crystal structure anatase phase. The increased diffraction peaks intensity of the TiO$_2$/SiO$_2$ confirms the improved crystallinity of the material. TiO$_2$/SiO$_2$ nanocomposite calcined at 800°C transforms into a rutile phase with a large crystallite size. FT-IR spectra justified the metal bond present as Ti-O-Ti, Si-O-Si, and Ti-O-Si. Due to the very fine anatase phase with a high crystallinity of the material, the absorption spectrum of TiO$_2$/SiO$_2$ nanocomposite can be calcined at 300 °C as a smaller band gap. On increasing the calcination temperature, the UV absorption peak shifts towards the higher wavelength. The absorption spectra of TiO$_2$/SiO$_2$ nanocomposite samples show an absorbance in the visible region, which was a good indication for the system being an effective photocatalyst in visible range or sunlight. The PL intensity of TiO$_2$/SiO$_2$ nanocomposite calcined at 300 °C has been split into many sharp peaks, which is due to good crystallization, thus reducing the recombination rate which causes a higher photocatalytic activity. While comparing, the degradation of both dyes, it is found that the same sample calcined at 300 °C exhibits a better photodegradation for MB (80-85%) than MO (70-75%) under visible light irradiation within the duration of 2 hours.

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Conflict of Interest
There is no conflict of interest.

Supporting Information
Not applicable.

References
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