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Hydrothermal Synthesis of Mesoporous TiO₂ Nanoparticles Using Pluronic Copolymer and EDTA: Synthesis, Characterization, and Photocatalytic Studies

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Abstract

The mesoporous TiO₂ nanoparticles were synthesized with Pluronic F-127 non-ionic copolymer and EDTA surfactant by hydrothermal method. The structural, morphological optical and photocatalytic properties of the TiO₂ nanoparticles were analyzed by X-ray diffraction, Raman spectroscopy, High Resolution Scanning Electron Microscopy, Transmission Electron Microscopy, BET surface area, UV-VIS absorption spectroscopy, photoluminescence spectroscopy, photocatalysis and decay time studies. The XRD and Raman spectroscopy confirmed the tetragonal anatase TiO₂ nanoparticles. Raman spectroscopy revealed the phonon modes characteristic to the anatase TiO₂ at 153.4, 204.7 and 638.2 cm⁻¹ is related to the E₁ vibrational modes, 394.6 cm⁻¹ for the B_{1g} vibrational mode and 512.6 cm⁻¹ attributed to A_{1g} mode. The optical absorption of the TiO₂ is centered at 360 nm. At this UV light excitation, the TiO₂ gives emission in the visible region, in which the emission at 427 nm is stronger than that occurred at 534 nm wavelength. FESEM examination showed the nanoparticles are agglomerated to form as spherical-nano clusters. TEM analysis shows that the average particle size of the prepared TiO₂ was measured to be 11 nm along with that SAED pattern shows the interplanar distance of $d_{(101)} = 0.342\text{nm}$. The BET nitrogen adsorption-desorption studies revealed a hysteresis loop consistent with type IV isotherm typical to mesoporous material. The BET surface area of the mesoporous TiO₂ nanoparticle is 45.043 m²g⁻¹ and the average pore diameter is 39 nm. The mesoporous TiO₂ nanoparticle with high surface area and pore size, the dye degradation studies showed an efficiency of 76%, and the results show that mesoporous anatase TiO₂ can be used for photocatalytic applications.

Keywords: Nanoparticle, TiO₂, mesoporous, XRD, Raman spectra, BET analysis

1.0 Introduction

The global energy demand has been fulfilled by non-renewable fossil fuel sources. [1] The energy requirement increases in modern society due to population growth, luxurious lifestyle and industrial development. Optical nanomaterials research is actively pursued across the globe [2] for photocatalysis and solar energy applications. The material of choice for solar cell applications is semiconductor silicon, III-V semiconductors, copper indium gallium selenide, transition metal oxides and lanthanide-doped materials [3-5]. The transparent conducting oxides are useful for various applications [6,7]. The TiO_2 , ZnO and SnO_2 semiconducting metal oxides have been largely investigated for solar energy [8,9] and TiO_2 nanoparticles for photocatalysis applications. [10,11]. Titanium dioxide exists in three mineral forms such as anatase, rutile and brookite. The nanoscale TiO_2 with a large surface area increases the dye adsorption and improves photocatalytic property. The metal oxide nanoparticles with extremely small size minimize the light scattering. A good strategy to increase the light-adsorption is to manipulate TiO_2 particles as sub-microsphere clusters and mesoporous structures.

TiO_2 nanoparticles have been synthesized by sol-gel, sonochemical, hydrothermal, microwave hydrothermal, solvothermal, spray drying, spin coating, evaporation-induced self-assembly flame pyrolysis and electrochemical methods. [12-15] Different kinds of synthesis methods have been explored to prepare TiO_2 nanoparticles. [16] The hydrothermal method is low-cost strategy to prepare mesoporous TiO_2 nanoparticles [17,18] by using surfactants. The surfactant acts as structure-directing agent to manipulate the size, surface area to volume ratio and porosity (micro, meso and macro) of TiO_2 . The structure-directing agents such as phosphates, ionic and non-ionic surfactants, amines and block co-polymers [19] have been used to synthesize mesoporous TiO_2 . A wide range of mesoporous materials have been prepared using a soft-template strategy using block copolymers. [20] It has been reported that Pluronic F127 triblock copolymer [poly (ethylene glycol)-block-poly-(propylene-glycol)-block-poly (ethylene glycol)] has the advantage of generating pores of larger dimensions. [21] The high molecular weight F127 surfactant templating agent possesses long hydrophilic polyethylene glycol (PEO) and hydrophobic polypropylene glycol (PPO) segments, which induce a thick wall in the formation and large pore diameters in the mesoporous structure. Apart from Pluronic copolymers, non-Pluronic block copolymers with hydrophilic blocks like poly (ethylene oxide), poly (2-vinyl

pyridine) or poly (4-vinyl pyridine) and hydrophobic polystyrene, polyisoprene and polyacrylonitrile can be used to make mesoporous nanoparticles. Mesoporous materials have excellent properties such as high specific surface area, large pore volume, tunable pore size and shape. The high surface area mesoporous material is beneficial as it gives a large number of active sites and hence it is advantageous for energy applications involving surface or interface-related phenomena like adsorption, catalysis and energy storage. The mesoporous materials with large pore volumes are beneficial to have a high loading of guest species like the dye molecules. Another important is the pore size which affects the mass transport of guest species. The large mesoporous (2 to 50 nm) could accommodate more active species than the microporous materials (less than 2 nm). Therefore, architecting materials with balanced control of particle size, surface area, pore size and pore volume are important to achieve the desired properties and performance. The mesoporous materials have been prepared by template-free, hard template and soft template methods. The template-free method usually involves metal-organic frameworks. Hard-templating methods utilize silica, carbon, or colloidal crystals. The soft template methods utilize small-molecule surfactants and block copolymers [22,23] and it is advantageous because the soft molecules can self-assemble into different variety of ordered nanostructures with controlled pore size and shape. Soft molecules like the F127 copolymer and polystyrene can be easily dissolved in water and other common solvents and can be pyrolyzed at high temperatures under an inert atmosphere. The hierarchically ordered macro-/mesoporous TiO_2 nanostructures of high surface area were prepared by using templates of macro-porous carbon scaffolds and Pluronic F127 copolymer for photocatalytic applications. [24] Mesoporous structured TiO_2 nanoparticles have been reported to enhance dye adsorption because of their high surface area. [25, 27] Mesoporous TiO_2 microspheres with large surface area and nanoscale pore size were synthesized by glycolate and hydrolysis-assisted process for photocatalytic reduction of CO_2 . [28, 29] have synthesized the mesoporous TiO_2 microspheres by self-assembly strategy using Pluronic F127 as template, Tetrabutyl titanate as precursor, Tetrahydrofuran as a solvent, hydrochloric acid as the coordination and acetic acid for cooperative assembly with Pluronic F127. Monodispersed mesoporous TiO_2 nanospheres were synthesized by oleic acid modification by hydrothermal method for visible light photocatalytic application. [30] The carbonate-doped mesoporous TiO_2 nanospheres of size 10 to 15 nm were prepared by two two-step solvothermal methods using hexadecylamine and ethanol for dye-sensitized solar

application. [31] In this work, the mesoporous TiO_2 nanoparticles were synthesized by soft template approach by using the Pluronic F127 copolymer structure directing agent and EDTA as surfactant by hydrothermal technique.

2.0 Materials and Synthesis

Titanium (IV) Isopropoxide (TTIP), Titanium chloride (TiCl_4), Hydrochloric acid (HCl), butanol, Tthylenediaminetetraacetic acid (EDTA) and Triblock copolymer poly (ethylene glycol)-block-poly-(propyleneglycol)-block-poly (ethylene glycol) (Pluronic F127, $M_{av} = 12,600$) were used in the present work. The schematic of the TiO_2 synthesis is shown in Figure 1. The Pluronic F127 co-polymer and EDTA were used as structure-directing agents and surfactants. Initially, acidified butanol was prepared by mixing a known amount of butanol and hydrochloric acid. The polymer template solution was prepared by dissolving the Pluronic F127 powder in an acidified butanol solution, which forms a colloidal gel. In one beaker containing the F127 gel solution, EDTA was added under vigorous stirring for 2 hours at room temperature. The template solution was prepared by using Pluronic F127 (0.01moles = 12.6g), Butanol (100ml) and EDTA (0.01moles = 0.292g). In another beaker, the titania precursor solution was made by mixing the TTIP (0.5M = 14.80 ml), TiCl_4 (0.5M = 5.481 ml) with Butanol (100 ml) and HCl (5 ml). Finally, this titania solution was added slowly into the Pluronic F127 template solution and stirred for about 12 hours at room temperature. The molar ratio between F127 and TTIP was kept at 0.01 M to 1 M. The entire solution mixture was aged for 48 hours and transferred into a Teflon-lined autoclave for solvothermal heat treatment at 180 °C for 24 hours. The thick paste as shown in the inset in Figure 1 was obtained. It was dried in a muffle furnace at 200 °C for 12 hours, ground into fine powder by agate-mortar and calcined at 450 °C for 2 hours in a muffle furnace. Due to the high amount of Pluronic F127 (12.6 gm) taken during sample preparation, the product appeared ash-colored clay-like paste. The polymer template was removed by calcination at 450 °C for 2 hours in a muffle furnace. It was ground to a fine powder in agate mortar. Finally, white color mesoporous TiO_2 nanoparticles were obtained and characterized.

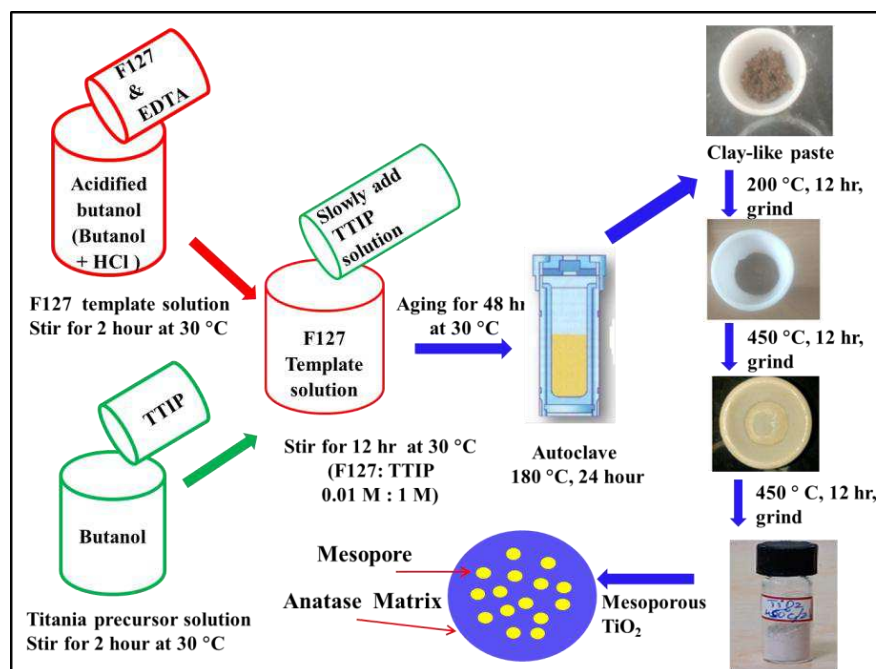


Figure 1: Schematic of the hydrothermal synthesis of mesoporous TiO₂ nanoparticles

3.0 X-Ray Diffraction Analysis

The crystal structural detail of the synthesized TiO₂ nanoparticle was analyzed using the X-ray powder diffractometer (BENCHTOP Rigaku Miniflex-600) with Cu-k α radiation ($\lambda = 1.5406 \text{ \AA}$). The as-prepared TiO₂ showed amorphous behavior, it became a polycrystalline phase by calcination at 450 °C (Figure 2). The characteristic diffraction peaks observed at three distinct 2θ positions of 25.265, 37.855 and 48.05° are respectively related to the (101), (004) and (200) planes of anatase TiO₂. The XRD patterns were analyzed by comparing with the standard powder diffraction file (JCPDS-73-1764) for tetragonal anatase TiO₂ and the lattice parameters are estimated to be $a = b = 3.78920 \text{ \AA}$ and $c = 9.53700 \text{ \AA}$ by indexing the data using XRDA software.

The crystallite size of the TiO₂ nanoparticle estimated by Scherrer's equation (1) is 9 nm

$$L = k \cdot \lambda / B \cdot \cos \theta \quad \square \square \square$$

where L is crystallite size, k is shape factor, λ is wavelength of X-ray, B is full width at half maximum and θ is diffraction angle. The crystallite size can also be estimated from the

Williamson – Hall (W-H) plot, which is based on size-broadening and strain-broadening effects. [32] The Williamson-Hall equation (2) is,

$$\beta_{\text{tot}} \cos\theta = C\epsilon \sin\theta + (K\lambda/L) \quad (2)$$

From the W-H plot shown in Figure 3, the crystallite size was calculated from the intercept of $K\lambda/L$ and the strain was calculated from the slope $C\epsilon$. In equation (2), K is the shape factor, λ is the wavelength of the X-ray beam, θ is the diffraction angle, β is the FWHM of peak (in radian), L is the crystallite size and ϵ is the strain. The estimated crystallite size and strain value are 12 nm and 0.00305 respectively.

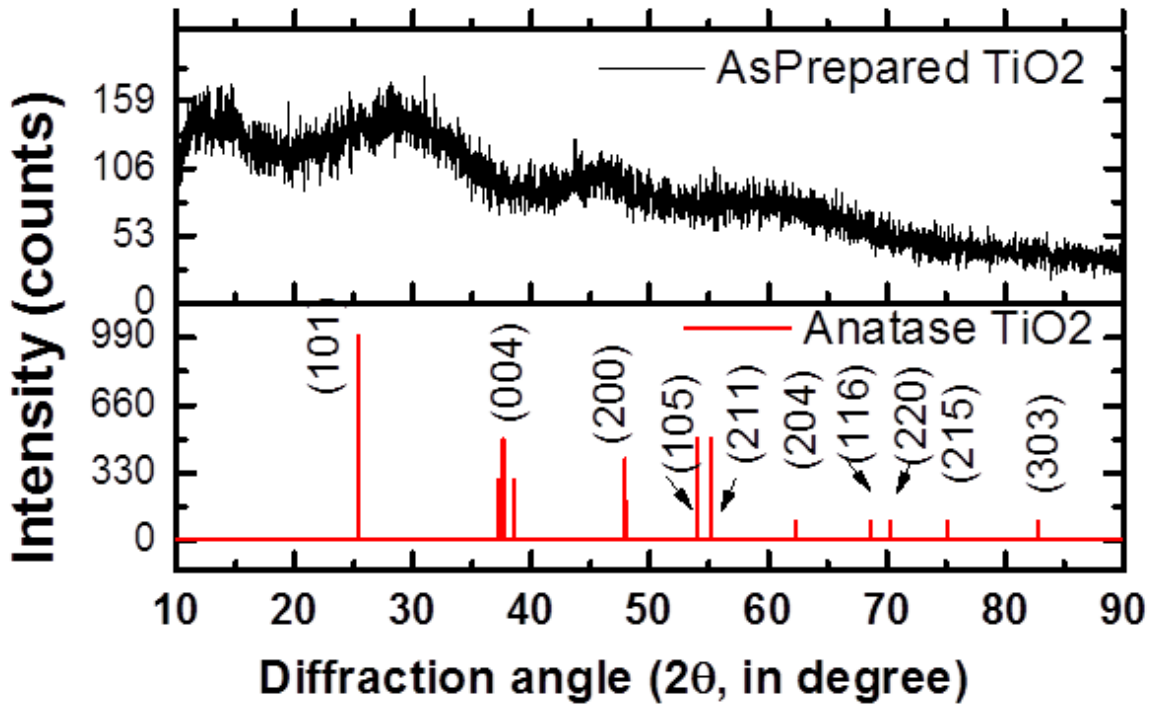


Figure 2(a): XRD pattern of as-prepared TiO₂ by hydrothermal method shows amorphous

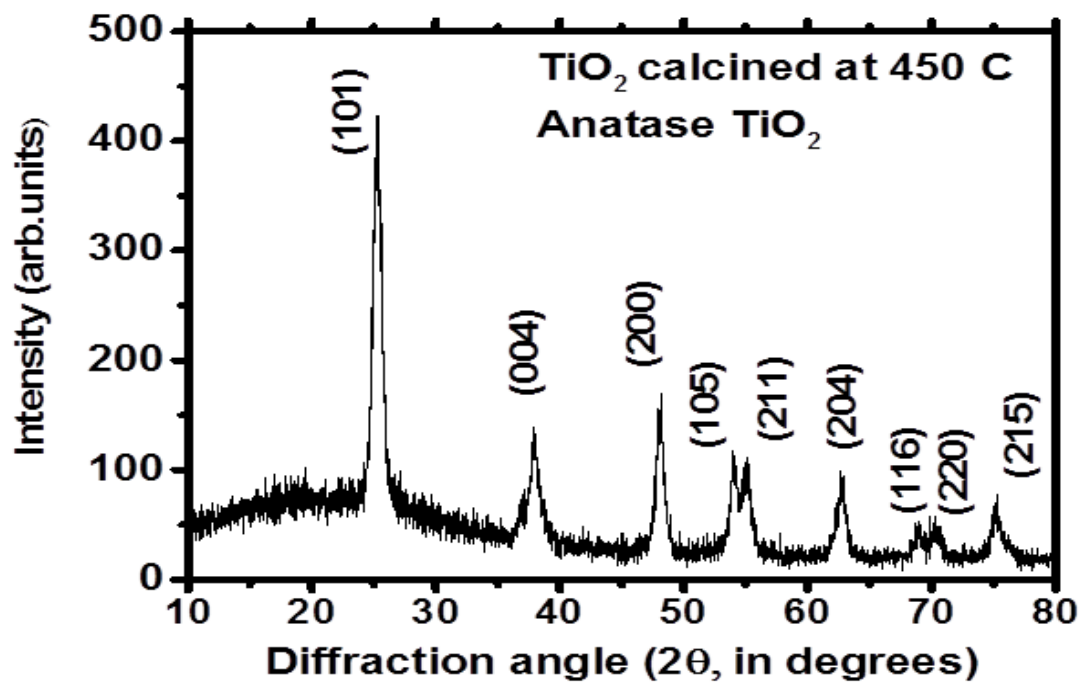


Figure 2(b): XRD pattern of the 450°C calcined TiO_2 shows anatase crystalline phase

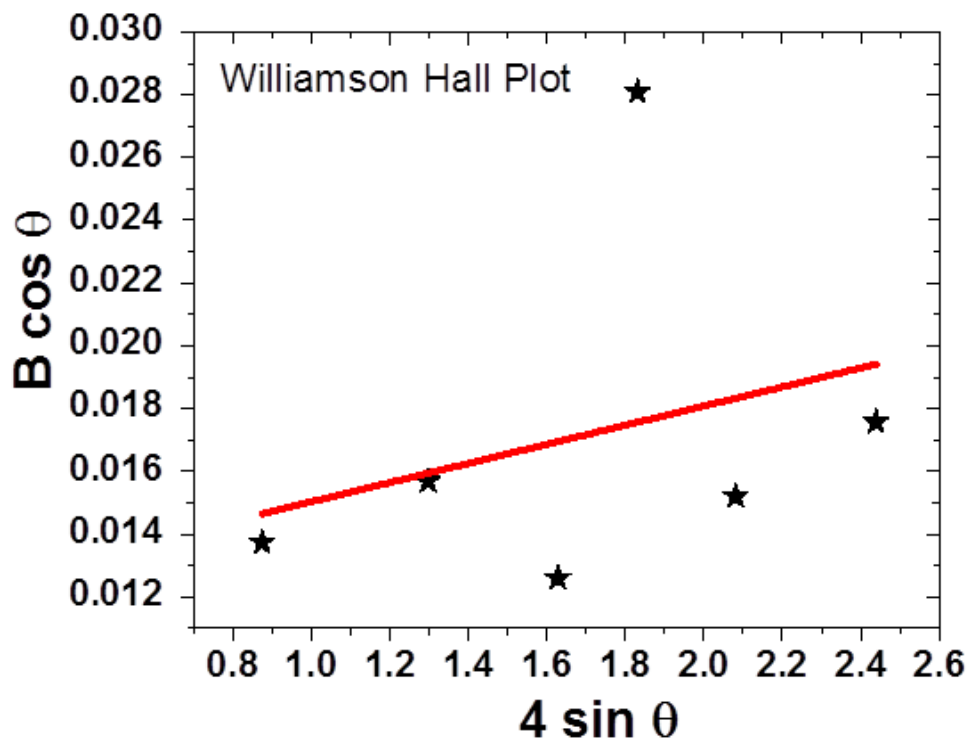


Figure 3: Williamson-Hall Plot of the TiO_2 nanoparticle

4.0 Raman spectra of TiO₂ nanoparticles

The structural details of the mesoporous TiO₂ nanoparticles were also studied using the Raman spectrometer (Horiba Xplore Plus) equipped with the Olympus BX-41 microscope (objective x100, x50, NA 0.9), TE cooled CCD detector (Synapse OE 1024x256), diode pumped solid state laser (532 nm), HeNe laser (632.8 nm) and 1200 gr/mm grating. The experiments were performed at laser power 10 mW with an acquisition time of 5 seconds. Three trials were registered to verify the sample homogeneity and absence of photo-induced phenomena. The diode-pumped solid-state laser at 532 nm was made to interact with TiO₂ nanoparticles. Raman spectrum was taken in backscattering configuration. The scattered light photons were collected from a small sampling area of 100 nm² with the help of an optical microscope (50X_VIS-LWD) attachment with a Raman spectrometer and TE-cooled CCD detector for analysis. All the measurements were carried out at ambient conditions. Before the measurement, the Raman spectrometer instrument was calibrated with Silicon as a reference at 532 nm and 632.8 nm. The Raman spectroscopy of Silicon showed a peak position at 520.6 cm⁻¹ (Supplementary).

Figure 4 shows the Raman spectrum of mesoporous TiO₂ nanoparticles calcined at 450 °C. It indicates crystalline structure and reveals a pattern characteristic of the anatase TiO₂. It is reported that the anatase TiO₂ has six Raman active modes. [33, 34] E_g at 144 cm⁻¹, E_g at 197 cm⁻¹, B_{1g} at 399 cm⁻¹, B_{1g} at 513 cm⁻¹, A_{1g} at 519 cm⁻¹, and E_g at 638.2 cm⁻¹. (Anatase = A_{1g} + 2B_{1g} + 3E_g). In the present study, the Raman spectrum shows a strong scattering localized at 153.4 cm⁻¹ due to the external vibration of the TiO₂ anatase structure. The Raman band at 153.4 cm⁻¹ is intense. The peaks at 153.4, 204.7 and 638.2 cm⁻¹ corresponds to the vibrational modes E₁. The peak at 394.6 cm⁻¹ could pertain to the B_{1g} vibrational mode. The Raman signal localized at 512.6 cm⁻¹ attributed to A_{1g} mode. The Raman bands for Rutile TiO₂ are not detected in the sample calcined at 450 °C.

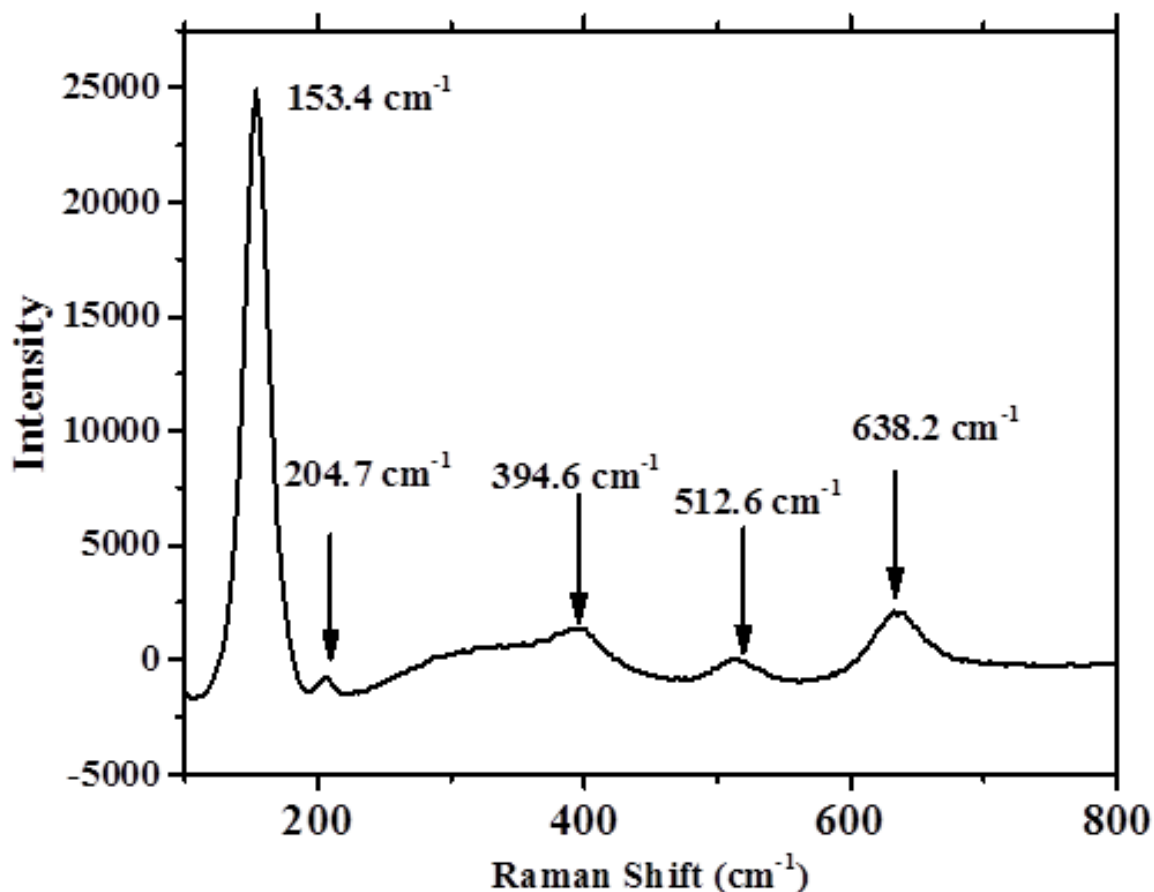


Figure 4: Raman spectrum of the mesoporous TiO₂ synthesized

5.0 Optical absorption and Photoluminescence:

Figure 5 shows the absorption spectra of the mesoporous TiO₂ nanoparticles. An absorption band is observed at about 360 nm. It can be assigned to the 3.2 eV band gap excitation of anatase TiO₂ that corresponds to the band-to-band transition from the valence band (O2p levels) to the conduction band (Ti3d level). The photoluminescence response of the TiO₂ nanoparticle was studied by exciting the aqueous solution of the TiO₂ nano-powder at 325 nm using a broadband Xenon lamp source with spectrofluorometer operated in double monochromator mode using 5 nm entrance and exit slit and the 1200 (Blaze 500) grating. The excitation wavelength was chosen at 325 nm (3.76 eV) as this energy equivalent is more than the band gap energy of bulk anatase (3.2 eV). The photoluminescence spectrum shown in Figure 6 indicates the emission peaks are centered at 400 nm (3.10 eV), 427 nm (2.90 eV) (strong) and 534 nm (2.32 eV) (weak). The 427 nm emission is stronger than the 534 nm emission. It has

been reported that 400, 427 and 534 nm emissions are assigned to the surface state due to the recombination of trapped electron-hole arising from dangling bonds (surface bonds) of TiO₂. The emission at 534 nm could be due to O²⁻ vacancies. Two main contributions to the PL of nanostructured anatase TiO₂, the “green” component around 2.3-2.5 eV (495–540 nm) are attributed to the presence of surface oxygen vacancies and the “red” component around 1.9–2.1 eV (600–650 nm) is due to the subsurface oxygen vacancies. [35] The visible luminescence band observed in the indirect band gap TiO₂ semiconductor could originate from oxygen vacancies associated with Ti³⁺. The photoluminescence of TiO₂ is a surface phenomenon. A change in the surface environment has a significant effect on the PL process. The ultraviolet light illumination gives a broad visible photoluminescence (PL) arising from the recombination of oppositely charged trapped and free carriers. The PL emission of anatase nanoparticles is due to the recombination of trapped electrons with valence band holes and it gives a broad spectrum with a peak in the red wavelength region. The higher energy emission could arise by the recombination of mobile electrons with trapped holes due to oxygen-vacancy color centers. Thus, the photoluminescence in TiO₂ is due to the recombination that depends on the spatial coincidence of trapped and mobile charges. It has been reported that the PL intensity is greater when transport is hindered for example in dense TiO₂ films used for gas sensing and lower when the charges are more mobile as in the case of sintered porous films used for solar energy conversion.

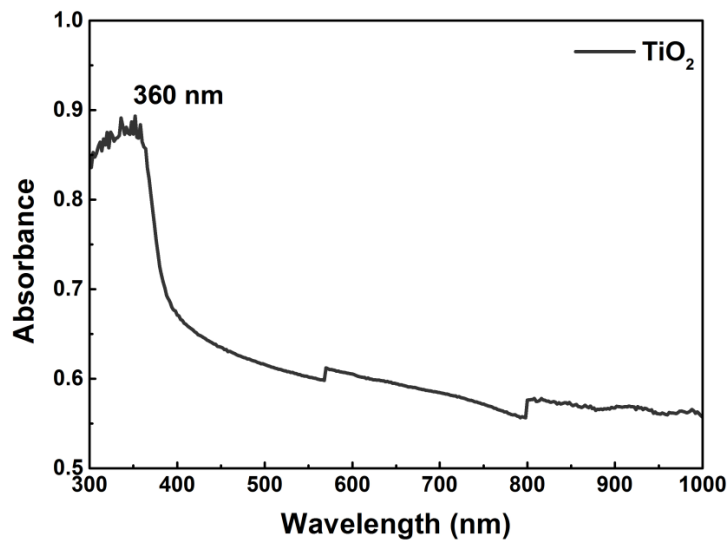


Figure 5: UV-Visible optical absorption spectrum of the mesoporous anatase TiO₂

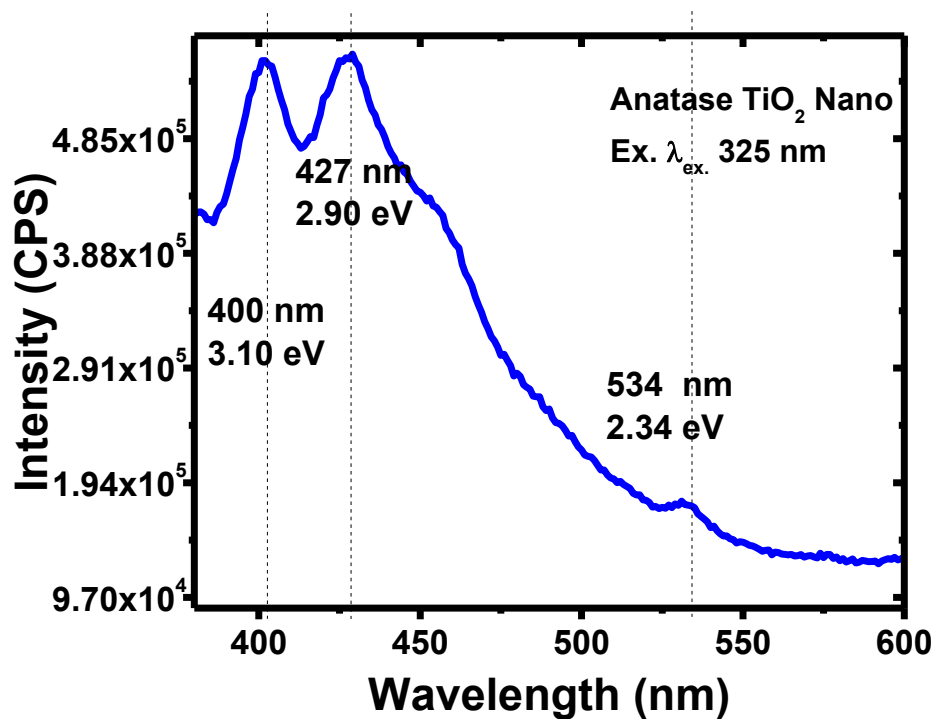


Figure 6: Photoluminescence spectrum of the mesoporous TiO₂ nanoparticle

6.0 FESEM Morphology and EDAX Analysis

Figure 7 (a-c) shows the morphology of TiO₂ nanoparticles prepared using the F-127 Co-polymer and EDTA surfactant. The low magnification FESEM Images in Fig.7a shows the TiO₂ nanoparticles are formed to be highly agglomerated. The high magnification images shows that spherical-shaped titania nanoparticles are formed as clusters (Fig. 7b,c). The particle morphology resembles the spherical buds stacked in the broccoli. Its individual particles are in the size approximately from 30 to 48 nm as shown in histogram (Fig. 7d). The EDAX analysis of the TiO₂ is shown in Figure 8 and the elemental mapping is in 9 (a,b, c). The strongest peak at 4.56 KeV which corresponds to Ti K α and 0.54 KeV peak related to O K α .

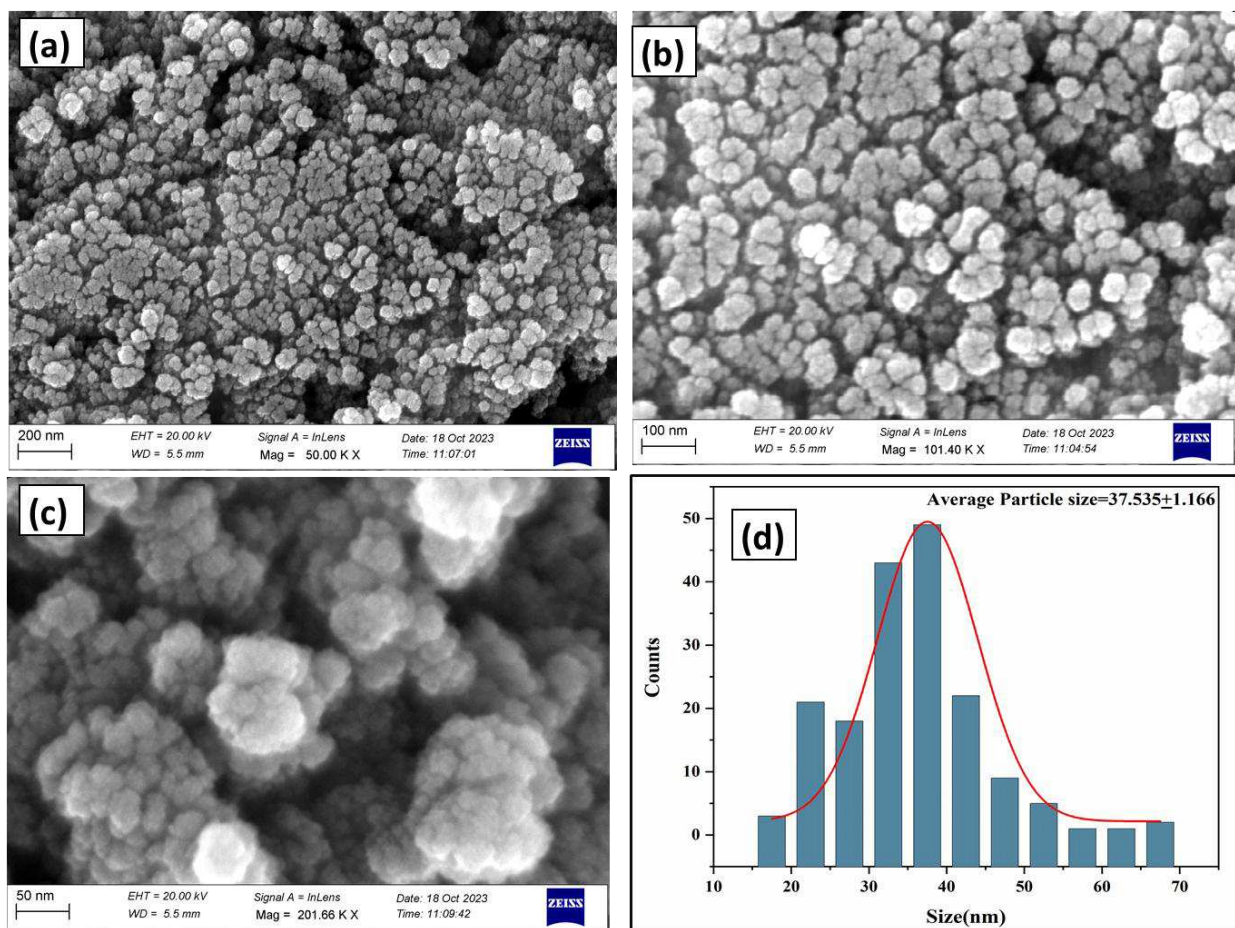


Figure 7. a-d. FESEM images of the TiO₂ nanoparticles prepared using F127 co-polymer and EDTA surfactant. The high magnification images (c) shows nanocluster morphology

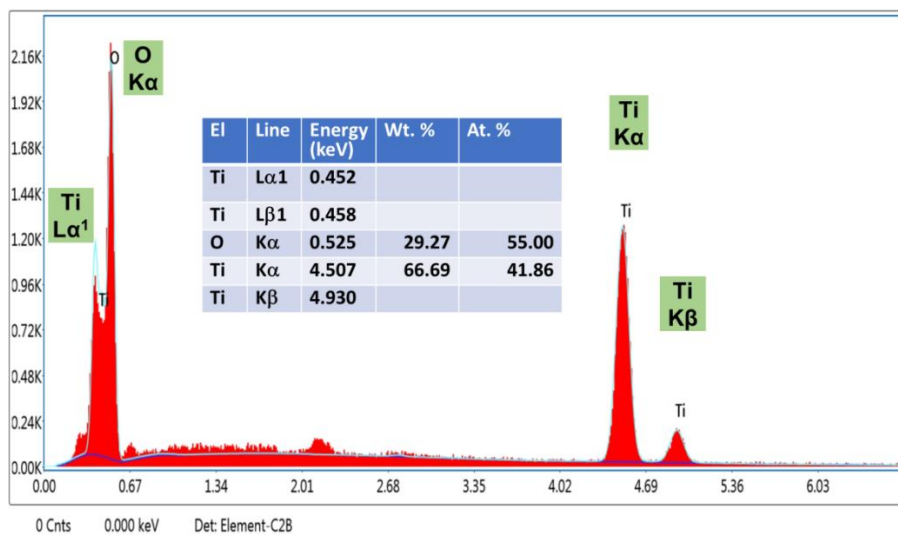


Figure 8 EDAX spectrum of the mesoporous TiO₂ nanoparticles

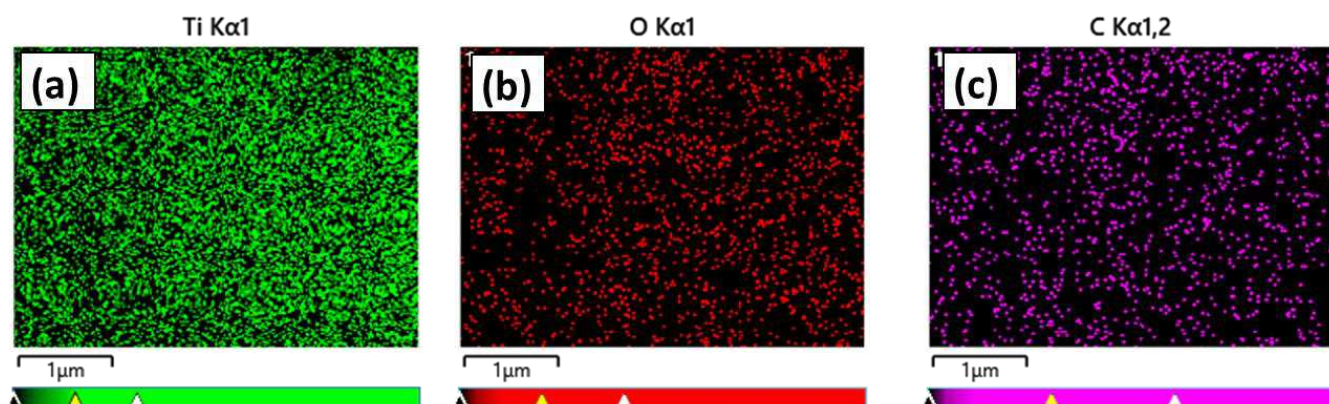


Figure 9 (a,b,c) EDS mapping of Ti, O and C in the synthesized TiO₂ nanomaterial

7.0 TEM Analysis

The morphology of the mesoporous TiO₂ nanoparticle was analyzed with the Transmission Electron Microscopy (TALOS F200S G2, Thermo Fisher Scientific, USA). HR-TEM images in Fig. 10 (a, c) indicate the formation of hexagonal-shaped Titania nanoparticles. The histogram (Fig. 10 b) shows an average particle size of 11 nm. It has been reported that hexagonal shaped anatase TiO₂ can be a candidate for visible light photo catalysis [36]. The TEM-EDAX shows the Ti and O peaks respectively at 0.52 and 4.5 keV (Fig.10d).

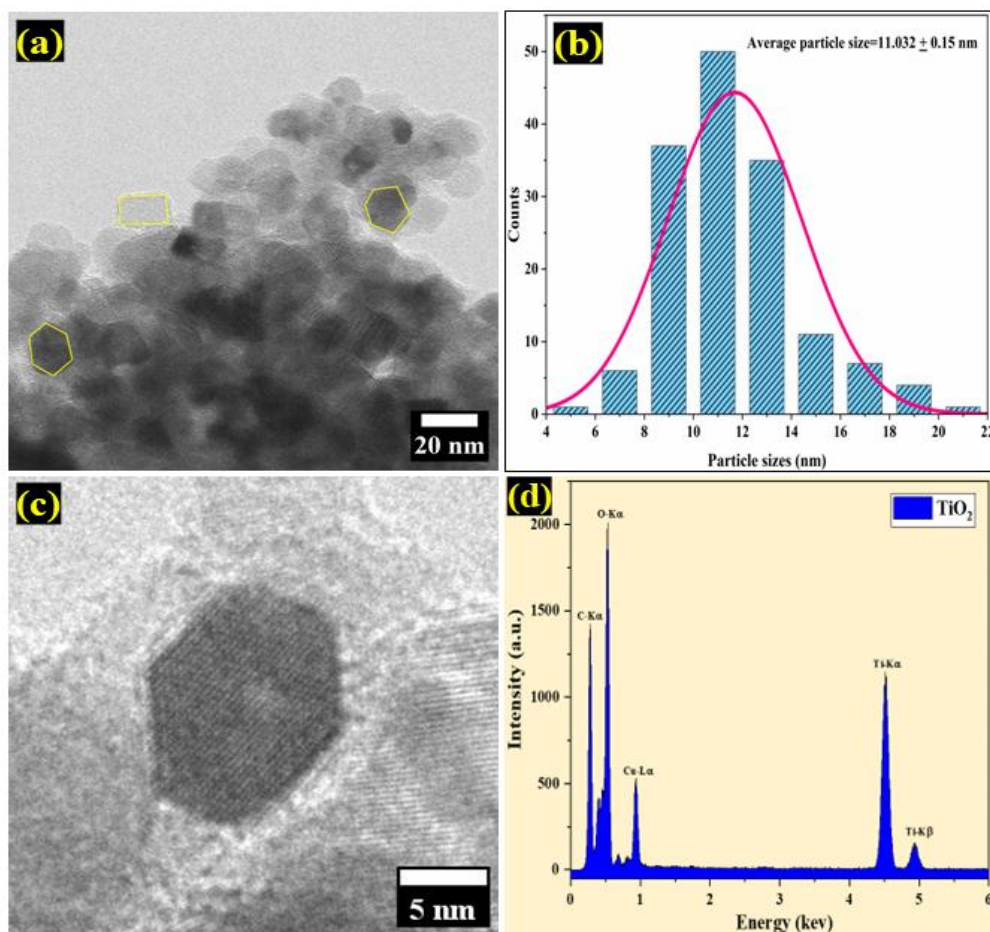


Fig 10. (a-c) HRTEM image shows the hexagonal shaped mesoporous TiO₂ nanoparticle, (b) particle size distribution and (d) the EDAX spectrum

A highly crystalline TiO₂ nanoparticle formation can be confirmed from the HRTEM image shown in Fig. 11 (a). The selected area electron diffraction (SAED) ring pattern shown in Fig. 11 (b) corresponds to reflections from crystallographic planes (101), (004), (200), (105), (116), (215) and (303) of anatase TiO₂. The result is in agreement with XRD pattern. The HR-TEM images show lattice fringe patterns of the TiO₂ nanoparticles (Fig. 11 c-d), in which the measured interplanar spacing of 0.342 nm corresponds to the (101) plane of the anatase TiO₂. The surface area and the volume of the hexagonal shaped TiO₂ nanoparticle was respectively calculated as 1144 nm² and 2526 nm³, from which the surface-to-volume ratio was estimated to be $0.41 \times 10^8 \text{ m}^{-1}$. The specific surface area of TiO₂ calculated to be 107.08 m²/g was obtained from the surface area divided by mass of TiO₂, which is higher than the value (45.043 m²/g) obtained from the BET analysis.

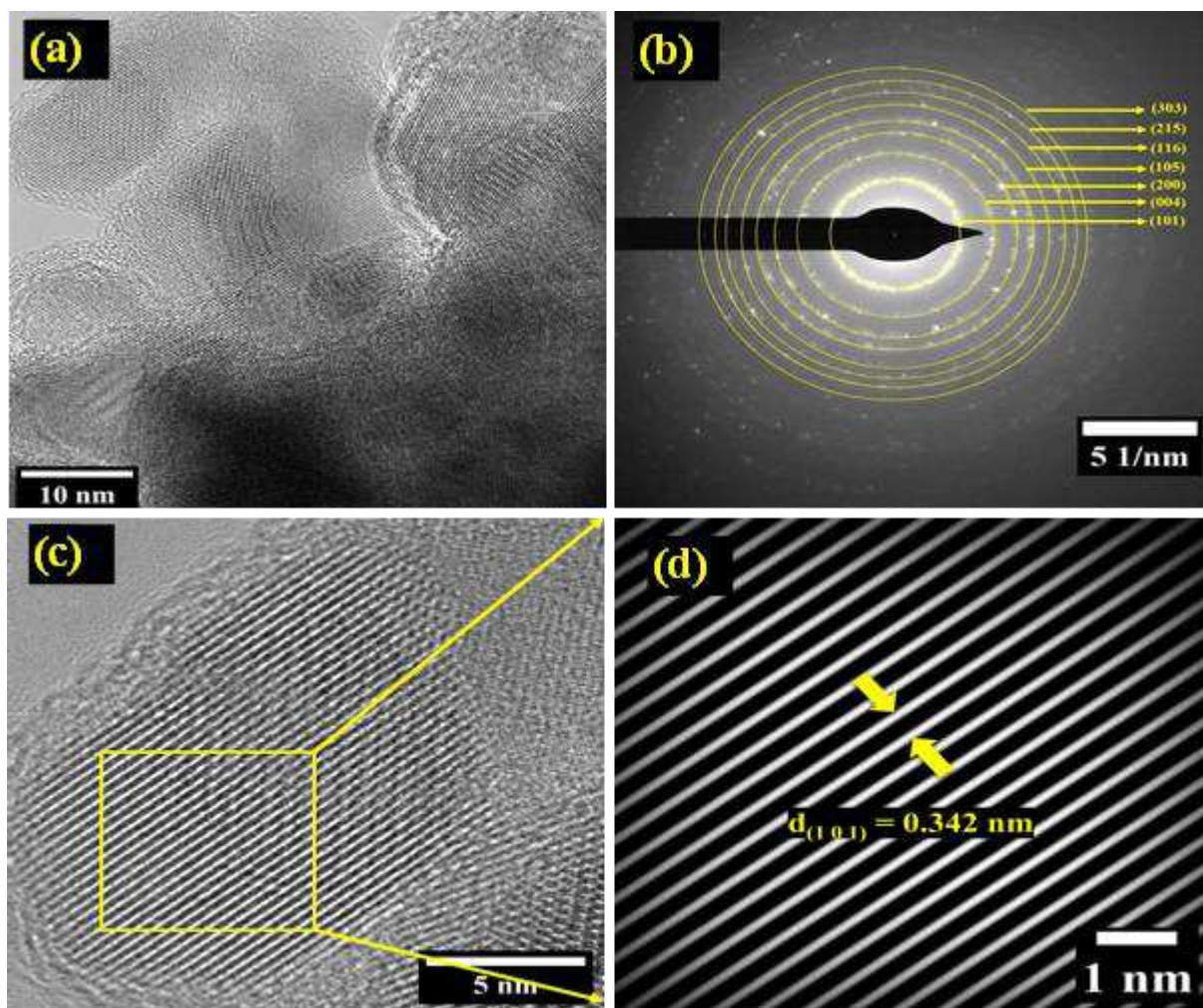


Fig. 11 (a) HRTEM images of the mesoporous TiO₂ nanoparticle Lattice fringe pattern and (c& d) at the magnified view, (b) SAED diffraction ring pattern

8.0 BET Surface Area and Pore Size Distribution

To evaluate the specific surface area, pore size and pore volume, nitrogen adsorption-desorption studies were carried out by the Brunauer-Emmett-Teller (BET) surface area analyzer (Micromeritics ASAPTM 2020, Accelerated Surface Area and Porosimetry System). The analysis was performed with nitrogen at a liquid nitrogen temperature of 77 K. Before the BET surface area measurement, 0.1176 g of TiO₂ powder sample was degassed in a vacuum at 150 °C for 19 hours to eliminate atmospheric gases, organics and adsorbed species present in the samples. The empty cell weighs 38.2697 g, the sample plus cell weight was 38.4015 g and after degassing it becomes 38.3873 g. The warm and cold free spaces were 23.4883 and 73.0348 cm³ STP atm⁻¹,

respectively. From the nitrogen adsorption-desorption isotherms the Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore size-volume were evaluated.

Figure 12 (a) shows the isotherm linear plot of the hydrothermal synthesized TiO₂ nanoparticles. The adsorption-desorption for relative pressure (P/P₀) exhibited hysteresis typical of mesoporous material. The adsorption-desorption isotherm coincides up to a relative pressure P/P₀ of 0.7, it steadily increases in the same path up to the P/P₀ of 0.8 and then the isotherm attains a separate path with an abrupt rise in volume of nitrogen adsorption. The hysteresis loop is consistent with the type IV isotherm characteristic of the mesoporous materials. The steady increase in isotherm can be related to capillary condensation of mesopores, which suggests homogeneity of the nanoparticle and indicates small pore size because the P/P₀ position of the inflection point is related to the pore dimension. The Pluronic F127 and EDTA-assisted hydrothermal synthesis of TiO₂ nanoparticle gives the BET surface area of 45.0432 m²/g which is larger than the value of 26.274 m²/g obtained in the sol-gel synthesized TiO₂ and Na doped TiO₂ [37] and 38.77 m²/g in the F127 synthesized TiO₂ [19] Therefore, the present synthesis resulted the mesoporous TiO₂ nanoparticle with large surface area could be useful for dye sensitized solar cell and photocatalysis applications.

In general, the pore size of materials is classified as micropore (less than 2 nm), mesopore (2 to 50 nm) and macropore (larger than 50 nm). Apart from BET surface area analysis, the pore size of the TiO₂ nanoparticles was measured by the BJH method, and the result is given in Table. Generally, pore size distribution is expressed in the pore volume (cm³/g nm) as a function of pore diameter (nm). Pore size distribution evaluation involves different mathematical concepts, the analysis gives discrepancies in the final results. The pore size can be estimated by three different approaches based on (i) incremental pore volume versus pore diameter (dV), differential pore volume versus diameter (dV/dD) and log differential pore volume versus diameter [dV/dlog(D)]. The researchers analyze the pore size distributions by any one of these methods. [38] Figures 12 (b and c) respectively shows the differential pore volume distribution curve (dV/dD) and log differential pore volume [dV/dlog(D)] distribution curve of the TiO₂ nanoparticle prepared by the Pluronic F127 copolymer. The dV/dD profile reveals information about both the smaller and larger pore sizes. But, log differential [dV/dlog(D)]

distribution shows the particles in larger pore sizes. The adsorption pore size distribution shows a very broad in the range from 5 to 100 nm centered at about 35 nm and the desorption pore size distribution shows a broad profile in the range 5 to 60 nm centered at 22 nm. The observed broad profile is typical of the trend of meso and macro-porous TiO_2 nanoparticles. It implies good expansion and contraction of pores respectively during adsorption and desorption, and such a large porous structure is beneficial to accommodate dye molecules for dye-sensitized solar cells and photo-catalytic applications.

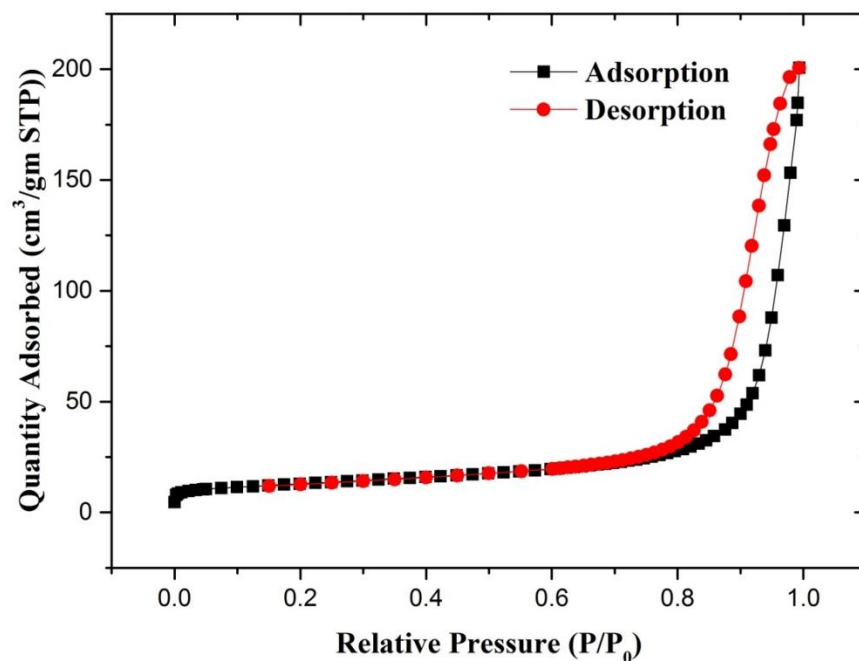


Figure 12 (a) Nitrogen adsorption-desorption isotherms of the mesoporous TiO_2 nanoparticles

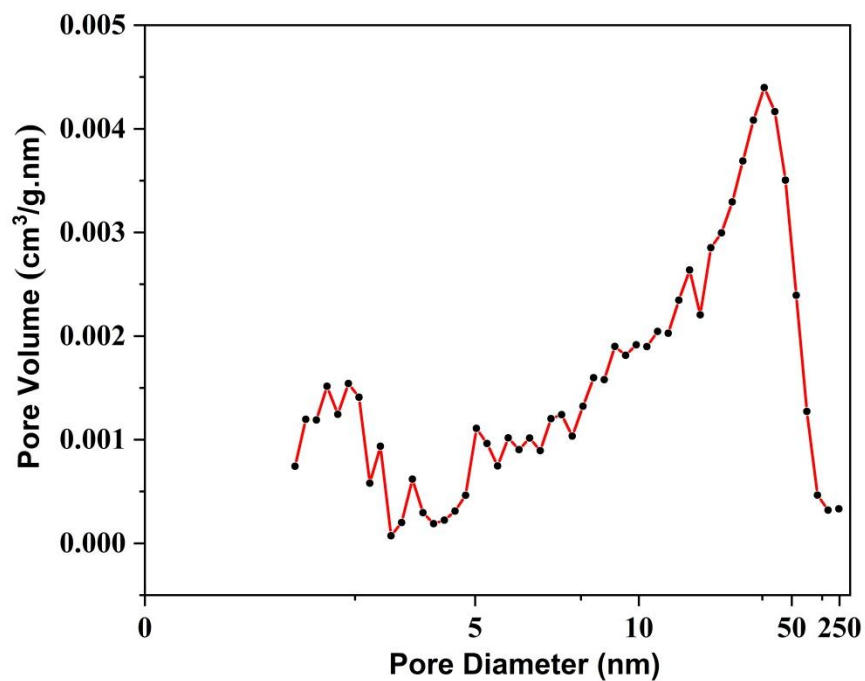


Figure 12 (b) BJH differential pore volume distribution curve (dV/dD) of the TiO_2 nanoparticle showing both the smaller and larger pore size distributions

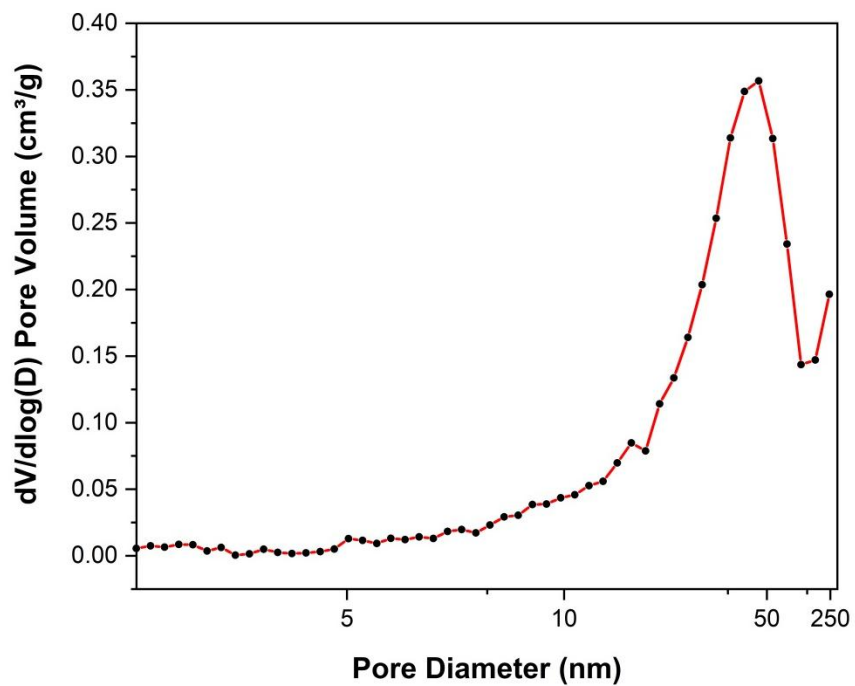


Figure 12 (c). BJH log differential pore volume distribution curve [$dV/d\log(D)$] of the TiO_2 nanoparticles particularly shows the larger pore size distributions

Table 1: Crystallite size, surface area, pore size and energy gap of the TiO₂ nanoparticle:

Crystallite size from XRD (nm)	BET Surface area (m ² g ⁻¹)	BET Adsorption average pore width (nm)	BJH Average Pore diameter from adsorption curve (nm)	BJH Average Pore diameter from desorption curve (nm)
9 to 12	45.043	27.55	34.88	21.85

9.0 Photocatalytic degradation of Methylene blue using TiO₂

The photocatalytic degradation was performed using the UV-visible spectrometer (SPECORD-210/Plus-Analytik Jena). For the photocatalysis experiment, the dye solution was prepared by dissolving 10 µl of methylene blue in 25 ml of distilled water. The 0.05g of the TiO₂ nanoparticles dispersed in 75 ml of distilled water was added with the dye solution and sonicated for 10 minutes. Under continuous stirring, the homogeneous dispersion was exposed to UV light irradiation (Philips UV Lamp Tube, 11 W). The dispersion was collected for every five minutes and its degradation behavior was analyzed by UV-visible spectrometer from the variation in the spectral light intensity. Initially, the absorption peak at ~657 nm was observed for methylene blue reference solution. The spectral intensity of the UV light exposed TiO₂-dye solution was measured.

The UV-VIS spectrum in Figure 13 (a) shows the photodegradation of methylene blue dye solution with TiO₂ under the exposure to a simple UV lamp tube light. Figure 13 (b) gives photographic evidence of the dye degradation using prepared mesoporous TiO₂ as the catalyst. A noticeable degradation was observed in 30 min and a complete degradation was achieved in 1 hour (Figure 13 c). Though the rutile and brookite TiO₂ exhibit direct bandgap behavior, the photocatalytic performance of anatase shows better photocatalytic activity, due to the indirect bandgap between valance and conduction band, reducing the recombination rate between photogenerated electrons and holes. Further, this facilitates generation of more hydroxyl species thus helping in achieving greater photocatalytic activity. Figure 14 illustrates schematic of photocatalytic mechanism of the mesoporous TiO₂ with methylene blue under UV irradiation.

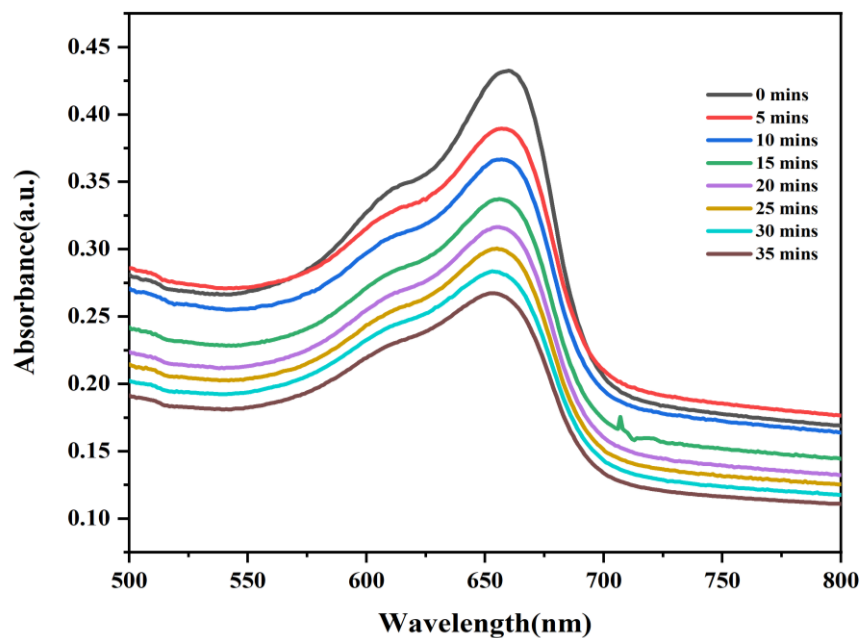


Figure 13 (a). UV-visible spectra shows the methylene blue dye degradation behaviour with the mesoporous TiO₂ nanoparticles

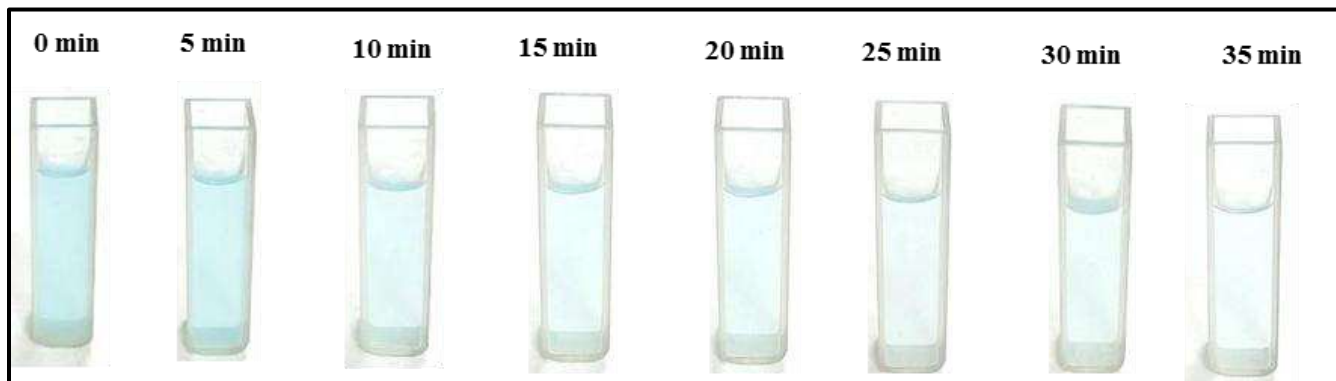


Figure 13(b) The sequence of photodegradation of methylene blue with mesoporous TiO₂ under UV irradiation for 30 minutes duration



Figure 13(c) The appearance of methylene blue before and after photo gradation under UV irradiation after one hour duration

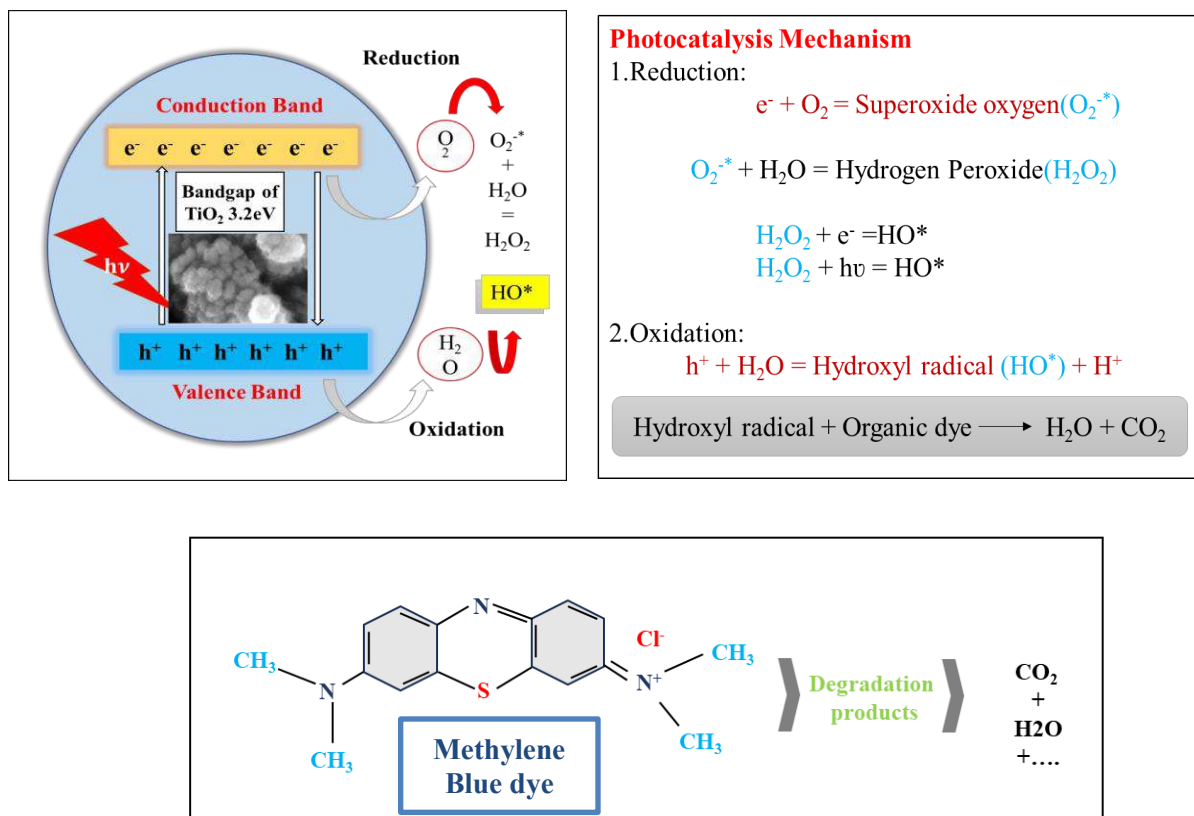


Figure 14 The schematic of photocatalytic mechanism of the mesoporous TiO₂ with methylene blue under UV irradiation

In semiconducting TiO₂ nanoparticles, when illuminated with UV light, the electrons excited from the valence band to the conduction band are involved in the process of reduction, by which oxygen (O₂) is reduced to superoxide ions (O₂^{•-}), these further react with the H₂O resulting in the formation of H₂O₂. The holes in the valence band oxidizes the H₂O molecules resulting in the formation of the hydroxyl radicals (HO[•]). These free hydroxyl radical species, produced due to reduction and oxidation help in the further oxidation of the chains of methylene dyes molecules and degrade them into simple other degradation compounds like CO₂ and H₂O.

10.0 Fluorescence Decay life time

The fluorescence decay time of the TiO₂ sample was measured using a Time Correlated Single Photon Counting system (TCSPC, Horiba instruments, USA) coupled with nano pulsed UV LED source. The sample was dispersed in water medium and excited with the pulsed nano LED at wavelength 310 nm with driving voltage of 1mV at 1 ns pulse width. The fluorescence

decay of electrons at 420 nm was measured which is shown in Fig.15. The obtained decay curve was fitted using double exponential function given by

$$I = A_1 \exp(-x/t_1) + A_2 \exp(-x/t_2)$$

Where, I is the fluorescence intensity, t_1 and t_2 is the fluorescence decay time components, A_1 and A_2 are amplitude components. The average decay life time can be calculated using the formula

$$t_{avg} = (A_1 t_1^2 + A_2 t_2^2) / (A_1 t_1 + A_2 t_2)$$

From the fluorescence decay curve fitted using double exponential function the average decay life time was found to be 16 ns. It is evident from the previous reports that the fluorescence decay lifetime of TiO₂ strongly rely on the pulse width of the pump source and its particle size. M.K.Singh. et.al (39) reported the decay lifetime studies of TiO₂ at different conditions where TiO₂ excited using a pumped flash lamp yielded decay life time of 3-4 ns whereas when excited using a pulsed led source the decay lifetime is reduces to the order of 10 ps to few nanoseconds. Fujihara et al. (40) and Harada et al. (41) also reported decay lifetime on the order of few nanoseconds when excited by a nanosecond pulsed source. The reason for this phenomenon is, when TiO₂ was excited using a pulsed laser or diode sources of small pulse width, the photogenerated electrons and holes were captured immediately by the trap sites. Because of the filled trap sites, the effective mobility of the charge carriers will improve leading to the accelerated electron-hole recombination. In contrast, when TiO₂ was excited using a flash lamp source, the photoinduced electrons and holes were initially captured by trap sites. The trapped charge carriers would then recombine either radiatively or non-radiatively, resulting in trap state emission and a slower decay rate in TiO₂ (42). Also, these trap states heavily influence the photocatalytic activity of the TiO₂. Since the photodegradation process is carried out in a steady state light source, the decay lifetime will be increased causing the electrons and holes trapped in the trap states to interact with water molecules to perform redox reaction causing the accelerated degradation of dye molecules. Thus, the trapped charge carriers with slow decay lifetime will be highly beneficial for improving the photocatalytic performance of TiO₂.

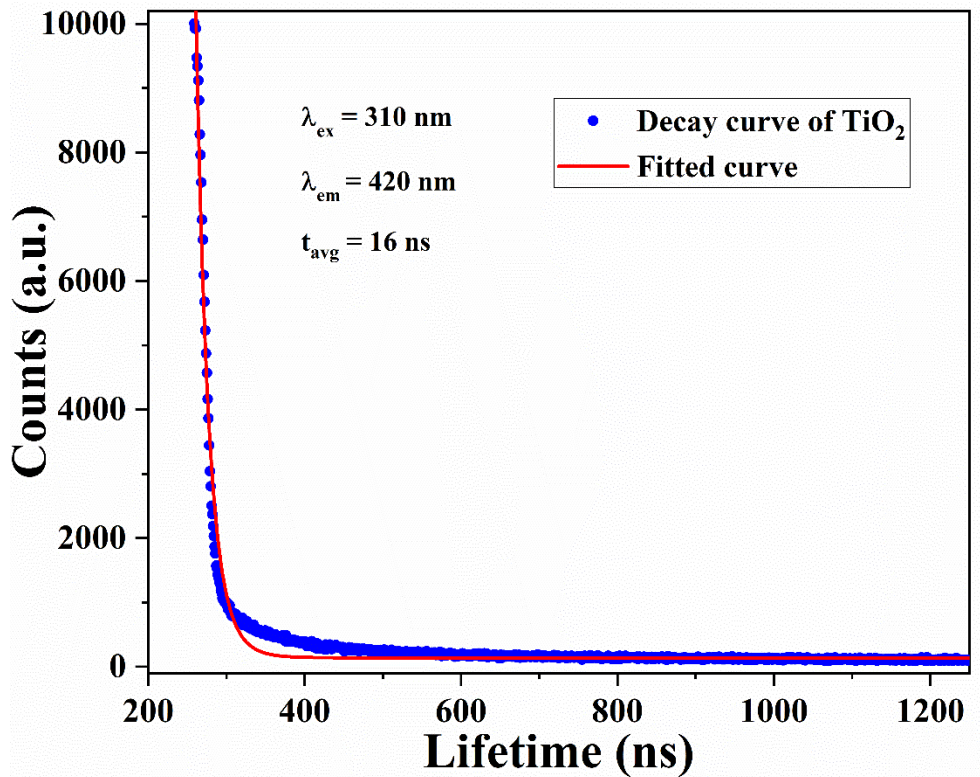


Figure 15 Decay time profile of mesoporous TiO₂ nanoparticle

CONCLUSION

The mesoporous TiO₂ nanoparticles were synthesized by using Pluronic F-127 copolymer and EDTA surfactant by hydrothermal method. The structural, optical absorption, photoluminescence emission, BET surface area and pore size were analyzed. The XRD powder diffraction and Raman spectroscopy confirmed the TiO₂ nanoparticle is formed in a tetragonal anatase structure. The crystallite size estimated by the Scherrer equation and Williamson Hall plot showed the value of 9 and 12 nm. The average particle size of the spherically distributed TiO₂ was found to be in the range from ~30nm to 40nm, through SEM morphology and further, the average particle size of the prepared Titanium nanoparticles was found to be 11.032 ± 0.15 nm through TEM analysis. The UV-Vis spectroscopy of TiO₂ showed optical absorption at 360 nm and photoluminescence emission at 427 and 534 nm. The mesoporous TiO₂ nanoparticles prepared by F-127 copolymer soft-template assisted hydrothermal synthesis give very small nano-crystallites of size 12 nm, a high surface area of $45.0432 \text{ m}^2 \text{ g}^{-1}$ and large pore diameter of 34.88 nm. The mesoporous TiO₂ nanoparticle with such a high surface area and pore

diameter can make it useful for photocatalytic applications, in this work degradation of methylene dye, was achieved with an efficiency of 76%, and the results show that mesoporous anatase TiO₂ could find its real-time applications.

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Conflicts of Interest:

The authors declare no conflict of interest.

Research Data Policy and Data Availability Statements:

All the data supported by the present research findings are included in this article. The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

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