Effect of electron irradiation to the photocatalytic activity of the titanium dioxide fibers

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Abstract. The main crystal phase of titanium dioxide (TiO₂) anatase, play the important role in the efficiency of photocatalysis. In this study, electron irradiation from 200-1,000 kGy has been used to alter the anatase-to-rutile phase ratio in TiO₂ particles. For photocatalytic reaction, the TiO₂ particles are loaded into the polymer fibers through electrospinning technique and then the ability of the fibers to photo degrade the methylene blue dye is measured. XRD analysis shows the changes in the crystal structure of the TiO₂ particles and the phase transformation from anatase to rutile after radiation. Morphology studies confirmed that the TiO₂ particles are incorporated well into the fibers and distributed homogeneously without beadings and agglomerations. The photocatalytic activity shows radiation at 1,000 kGy possess the highest degradation of methylene blue dye, resulting from the highest anatase phase content.

1. Introduction
Titanium dioxide (TiO₂) has been widely used as pigments, adsorbents, catalyst supports, filters, coatings, and dielectric materials [1]. In recent years, researchers are more focused on the use of TiO₂ semiconductors for photocatalytic activities with huge potential photovoltaic applications since TiO₂ has the properties of chemical stability, low toxicity, and low pollutant load [2]. The crystal phase of TiO₂ plays the important role in the efficiency of photocatalysis. TiO₂ exists in three different crystal forms; rutile (tetragonal), anatase (tetragonal) and brookite (tetragonal), with rutile is the most stable phase [3]. Among them, anatase phase has the most excellent photocatalytic activity compared to the others [4]. The rutile phase usually exhibits less activity than that of the anatase because of its lower surface affinity and a higher rate of recombination of photogenerated charge pairs [5]. However, the mixture of anatase and rutile TiO₂ offers a better effect on carrier transfer in photocatalytic applications, because the close contact between the anatase phase and rutile phase contributes to a smooth transfer of charge between the two phases [6]. This behavior has been shown by P25 TiO₂ powder which contains 20% rutile and 80% anatase, and it has good photocatalyst properties [7].

The photo-response and photoactivity of TiO₂ relies on the energy bandgap (Eₘ) of the material. TiO₂ is basically a poorly visible light absorber with Eₘ is around 3.2 eV, however, for an efficient photocatalytic reaction to take place, TiO₂ requires Eₘ comparable to the energy of the photons of the visible light which is less than 3.0 eV. A various approach has been done to improve the photo-
response and photoactivity of TiO$_2$. One of the well-established methods is utilizing the high energy electrons to alter the $E_g$ properties of the TiO$_2$. This method utilizes the accelerated electrons generated by electron beam accelerators without the use of radioactive isotope. Previous study has shown that the $E_g$ of TiO$_2$ powder was altered depending on the amount of electron irradiation dose. At a low dose of irradiation (between 4-20 kGy), the direct $E_g$ decreases from 3.33 eV to 2.4 eV while after a high dose of irradiation exposure (between 100 – 1,000 kGy), the direct $E_g$ increases from 3.0 eV to 4.0 eV. These results also showed that anatase transformed to rutile at high dose irradiation with the ratio of 20:80 (anatase:rutile) at dose of 700 kGy [8]. This phase transformation is occurred due to the presence of $\delta$ (O-Ti-O) bending mode of rutile in irradiated TiO$_2$ that led to the oxygen vacancies [9].

Besides the crystal phase and the energy band gap ($E_g$), the efficiency of photocatalysis is also depends on the surface properties of TiO$_2$. It is because the photocatalytic reaction takes place only when photoinduced electrons and holes are available on the surface [10]. Commonly, TiO$_2$ is used as bulk form whereby TiO$_2$ powder contains nanoparticles dispersed in solution to form a suspension. When used in suspension, TiO$_2$ aggregates rapidly due to its small size (4 nm to 30 nm) and its aggregates may cause scattering of the light beam resulting in loss of catalytic efficiency [11]. In addition, it is a must to separate the powdered TiO$_2$ after the photocatalytic reaction is completed to recover the catalysts. This post treatment separation is normally difficult and energy consuming, thus it is impractical for use in water-treatment plants [12]. To solve these problems, the TiO$_2$ particles were immobilised on solid supports to ease the post-treatment problems and to facilitate the renewable use of the catalyst [11]. To immobilize the TiO$_2$ particles, it can be assembled onto different substrates and fabricated into different types of thin films [12,13].

In this study, TiO$_2$ was bounded in a polymer fibers which is prepared via electrospinning technique, to prevent its particles aggregated. The advantage of fibrous photocatalyst is to have a high surface-to-volume ratio and 3-dimensional open structure that provides more surface actives for photocatalytic reaction to occur [14]. Recently, Riaz et al. has proved that the TiO$_2$ nanofibers calcined at 650°C, with the anatase/rutile phase ratio of 83:17 exhibited the best photocatalytic performance under UV irradiation [15]. Ismaya et al. found that the addition of TiO$_2$ nanoparticles in the polymer solution decreases the solution viscosity and increases the conductivity of the fibers. The decrease in fiber diameter will help in the increment of the active site thus increase the photocatalytic ability of the fibers [16]. Nevertheless, Ismaya et al. only considered the relationship between the ratio of anatase: rutile and photocatalytic activity, but not focus on the distribution of TiO$_2$ on the surface of the fiber. In this work, we prepared the polymer fibers using electrospinning method loaded with TiO$_2$ nanoparticles with different anatase:rutile ratios. The objective of the work is to study the photocatalytic reactions of the TiO$_2$ fibers and discussed the performance with regards to the crystal phase structure of TiO$_2$ adjusted by electron irradiation.

2. Materials and methods

In this study, the readily synthesized TiO$_2$ particles were irradiated with a 3 MeV electron beam (EPS 3000) at a dose in the range of 0 kGy to 1,000 kGy. After irradiation, the TiO$_2$ powder was characterized using the X-ray diffractometer (XRD, XPert Pro MPD, Ag-K$\alpha$ irradiation, $\lambda= 0.561 \, \text{Å}$) for phase and crystallinity studies.

2.1. Preparation of titania fibers by electrospinning

The TiO$_2$ fibers were prepared using the electrospinning technique. A known amount of irradiated TiO$_2$ powder and surfactant were mixed together and stirred in 3 ml of deionized water before being ultra-sonicated for 3 hours. After that, PVA powder was added into the sonicated solution and stirred for 20 minutes at 80 °C yielding a milky viscous solution. The solution was transferred to the plastic syringe and the needle was connected to a high direct current (d.c) voltage at 15 kV and ground to a metal plate, covered with aluminum foil. The electrospinning was done at room temperature and the TiO$_2$ fibers were collected on the aluminum foil at the working distance of 14 cm. The rate of the spinning was 0.03 ml/h. The morphology of the fibers were then characterized using field emission
scanning electron microscope (FESEM, GeminiSEM 500, Carl Zeiss) and the titanium (Ti) element was determined using energy dispersive X-ray (EDX, X-Max 80, Oxford Instrument) that attached to the same microscope.

2.2. Experiment for photocatalytic activity of titania fibers
Methylene blue (MB) dye was used as a reference to the organic pollutant to study the photocatalytic activity of TiO$_2$ fibers. Prior to the photocatalytic experiment, the calibration curve for MB dye solution with concentration of 1 ppm to 5 ppm was generated and the R$^2$ obtained was 0.996. A 12.25 cm$^2$ sheet containing TiO$_2$ fibers was placed flat in a 100 mL beaker and each beaker was filled with 50 mL of MB solution of 2.5 ppm. The beakers were then placed 12 cm away from the UV light source (400 watts) in a black box. During the experiment, a sample solution of 5 mL was taken at interval of 30 minutes for 2 hours and every hour for 5 hours. The concentration of the MB dye solution was measured with the UV-Vis spectrometer (Lambda 35, Perkin Elmer).

3. Results

3.1. Phase characterization
The XRD was used to study the phases present in TiO$_2$ powder, PVA fibers and TiO$_2$ loaded PVA fibers (TiO$_2$ fibers). Figure 1(a) shows the diffraction patterns for TiO$_2$ powder before and after electron irradiation. In the TiO$_2$ powder, there are two phases present which are anatase (ICSD: 01-070-6826) and rutile (ICSD: 01-083-2242). The peaks at 2$\theta$ = 9.077°, 2$\theta$ = 13.545°, 2$\theta$ = 16.970°, 2$\theta$ = 19.129°, and 2$\theta$ = 21.735° correspond to the anatase phase. An intense peak at 2$\theta$ = 15.704° corresponds to the rutile phase for non-irradiated TiO$_2$ powder. As the irradiation dose increased to 200 kGy, all peak intensity reduces and become stable up to 800 kGy irradiation. The increase in the irradiation dose from 200 kGy to 800 kGy does not give in a significant change towards the number of peaks and phase present. Figure 1(b) shows the comparison of diffraction patterns for TiO$_2$ fibers and PVA fibers respectively. For TiO$_2$ fibers, the peaks are identified at 2$\theta$ = 25.8°, 38.15°, 48.53°, and 55.13° which can be indexed to (011), (020), (015), and (024) plane respectively. This pattern is identified as anatase phase (ICSD: 01-070-6826) that has a tetragonal structure. The broad peak at 2$\theta$ = 25.8° is also observed on the pure PVA fibers, indicates that there is texturization occurred during electrospinning process [17]. Texturization is a mechanism of PVA changed its crystal structure to a preferred orientation to accommodate the presence of TiO$_2$ and surfactant during electrospinning process [18].

![Figure 1](image-url) **Figure 1.** (a) XRD spectra for TiO$_2$ powder irradiated with electron at doses of 0 kGy to 800 kGy; (b) XRD spectra for pure PVA fiber and TiO$_2$ loaded PVA fiber.
From XRD data, the crystallite size of the phase present was estimated using the Debye-Scherrer equation given by Equation 1:

\[ t = 0.9 \lambda / \beta \cos \theta \]  

(1)

where \( \lambda \) is the X-ray wavelength, \( \beta \) is the full-width half maximum (FWHM) of the peak and \( \theta \) is the Bragg’s angle.

The crystallite size of the phase present is as tabulated in Table 1. Based on the calculated crystallite size, for the rutile phase, it can be observed that the crystallite size decreases for 0 kGy to 400 kGy samples and increases for samples of more than 400 kGy and the opposite occur for anatase phase. There is only a small difference in the ratio between anatase and rutile phase for different irradiation dose samples. The reduction in crystallite size by electron beam irradiation process plays an important role as it can allow the TiO\textsubscript{2} to be incorporated well in fibers and provide a larger surface area to volume ratio for the photocatalytic reaction to occur [19].

Table 1. The crystallite size of anatase and rutile phase irradiation process with different doses.

| Dose (kGy) | Crystallite size (nm) | Anatase:Rutile |
|------------|-----------------------|---------------|
|            | Anatase | Rutile |               |
| 0          | 9.4     | 45.5   | 68:32         |
| 200        | 11.0    | 36.4   | 65:35         |
| 400        | 10.6    | 25.9   | 63:37         |
| 600        | 9.1     | 30.3   | 69:31         |
| 800        | 7.9     | 38.5   | 76:24         |
| 1,000      | 12.1    | 17.0   | 80:20*        |

* value obtained from Rohaida C.H C et al. 2019 AIP Conf. Proc. 2068 020010 [9].

3.2 Morphology studies and elemental analysis

The morphology of the fibers is observed using FESEM. Figure 2(a) and 2(b) shows the FESEM images of a pure PVA fiber and TiO\textsubscript{2} fiber respectively. Both fibers are randomly oriented with no beadings are visible. Morphology of the pure PVA fiber is clear and smooth surface and the average diameter is 197 nm. Meanwhile, morphology of TiO\textsubscript{2} loaded fibers is uneven surface, and the average of its diameter is 393 nm, about double the size of PVA pure fibers. The presence of TiO\textsubscript{2} particles in the PVA solution is believed to increase the viscosity and the conductivity of the solution, thus produce larger size fibers [21]. The good thing is surface of the fiber does not show any agglomeration of TiO\textsubscript{2} particles indicating the nanoparticles were well dispersed on the fibers. Figure 2(c) shows at 100,000 times magnification, the surface looks porous and homogeneous, indicating the well dispersion of TiO\textsubscript{2} nanoparticles on the fibers’ surface.
Figure 2. FESEM images (a) Pure PVA fibers, Scale: 1.0 µm, (b) TiO$_2$ loaded fibers, Scale: 500 nm, (c) TiO$_2$ loaded fibers, Scale: 200 nm.

Spot elemental identification using EDX was performed on the fibers to identify the presence of titanium (Ti) and other elements and to determine their concentration (weight percent, wt%) throughout the fibers. Figure 3(a) illustrates the 2 different spots were chosen to identify the concentration (wt%) of Ti; spot 30 and 32 which represents location on the fiber and outside of the fiber respectively. From the EDX spectra shown in Figure 3(b) and (c), the concentration of Ti is determined at 16.23 wt% at the outside of the fiber and 6.22 wt% on the fiber itself. This indicates that not all TiO$_2$ nanoparticles is incorporated into fiber during electrospinning. The free particles are restored on the surrounding of the fibers. To check the distribution of TiO$_2$ particles on the surface of fibers, spot elemental identification was carried out at 4 different spots (spot 1, 2, 3 and 4) on one of the fiber as shown in Figure 3(d). Graph in Figure 3(e) shows there are 4 elements presence on the fibers’ surface; carbon (C), oxygen (O), titanium (Ti) and sulfur (S). Sulfur is basically from the surfactant. The graph indicates that the concentration of each element at the 4 different spots. The wt% of Ti in each spot is in the range of 15.26 to 18.08 wt%, almost identical to each point. These results proved that the TiO$_2$ particles are distributed homogeneously throughout the fibers.
3.3 Photocatalytic activity of titania fibers
The concentration of the methylene blue (MB) dye after the photocatalytic reaction was determined using absorbance measurement with UV-Vis spectrometer. Figure 4(a) and 4(b) show the concentration of MB dye decrease significantly over time in all fibers for 2 and 5 hours respectively. Figure 4(b) shows that the decrement is very rapid for the first one hour and then gradually decrease afterwards. This result is similar to the one that reported previously whereby a rapid increase in photocatalytic degradation of methylene blue in the first 30 minutes of the experiment and becomes slower after the next 30 minutes [22]. Figure 4(c) shows that the fibers loaded with 1,000 kGy irradiated TiO$_2$ exhibited the highest percentage of dye degradation which is 78.4% from the initial concentration after 2 hours. This is followed with fibers loaded with 800 kGy irradiated TiO$_2$ which shows degradation of 77.4%. For fibers loaded with TiO$_2$ irradiated at 200 - 600 kGy, the percentage of degradation is about the same to the non-irradiated TiO$_2$ loaded fibers. This means that, TiO$_2$ irradiated at above 800 kGy provide improved photocatalytic reaction than the others, which corresponds to the crystal phase of the TiO$_2$ after irradiation as shown in Table 1. At 800 and 1,000 kGy of irradiation dose, the ratio of anatase:rutile in TiO$_2$ is 76:24 and 80:20 respectively, indicating that TiO$_2$ with the highest anatase content possessed the highest degradation of MB dye. These results proved that the anatase:rutile phase ratio is important for photocatalytic performance as reported by previous researches that the mixed-phase TiO$_2$ with a higher amount of anatase exhibit a higher photocatalytic reaction than the individual phase either rutile or anatase [23].

![Figure 4](image_url)

**Figure 4.** The photocatalytic reaction of fibers (a) the degradation of MB dye solution in 2 hours, (b) the degradation of MB dye solution in 5 hours, (c) the percentage of MB dye degradation after 2 hours.

4. Conclusion
The electron irradiation on TiO$_2$ powder from 200 to 1,000 kGy dose leads to the changes in the crystallite size as well as the anatase-to-rutile phase ratio. TiO$_2$ particles are successfully incorporated into PVA fibers. The irradiation dose does affect the photocatalytic activity of TiO$_2$. 1,000 kGy dose exhibit the highest degradation of MB dye which is nearly 80% in 5 hours of immersion time, attributed by the highest anatase phase content in this sample. Therefore, the amount of electron irradiation dose modifies the crystallite size of TiO$_2$, hence change the anatase-to-rutile phase and as a result affect the photocatalytic reactions when exposed to UV light.

5. References
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