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Polyvinyl Alcohol/Titanium dioxide Fibers Prepared Via Electrospinning Methods for Potential Application of Water Treatment

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ABSTRACT

Titanium dioxide (TiO_2) is an ideal photocatalyst because of its stability in terms of chemical and optical properties. The performance of TiO_2 as fiber incorporated in a membrane may be better than in bulk form, especially in applications of water treatment. There are many methods for fabrication of TiO_2 in a composite membrane, such as freeze-drying, thermal evaporation, and physical and chemical vapor deposition. Unfortunately, these methods are not favorable because they require multiple steps, which may produce impurities. Electrospinning is a simple and versatile technique to produce a composite membrane comprised of TiO_2. In this study, we propose the fabrication of PVA/TiO_2 composite membrane using the electrospinning method for its potential in water treatment. We studied 2 parameters, which are polymer loading and sonication time, to investigate the quality of the electrospun fibers. Morphology and x-ray diffraction analysis showed that the TiO_2 particles were well incorporated into the PVA fibers. The ability of these electrospun composite fibers to degrade methylene blue dye under UV exposure confirmed that the PVA/TiO_2 fibers can be used in water treatment applications.

Keywords: TiO_2, electrospinning, fiber, photodegradation, membrane

INTRODUCTION

Titanium dioxide (TiO_2) becomes the most promising photocatalyst due to its advantages of being stable as catalyst, reasonably inexpensive, and relatively easy to produce and use.[1] It is human and environmentally friendly and can be used to treat polluted air and split the water to generate hydrogen.[2] Photocatalysis occurs when nano-TiO_2 is dispersed in an aqueous solution exposed to ultraviolet (UV) light, which causes a hydroxylation reaction that is initiated by hydroxyl radicals (*OH).[3-9] Under UV light illumination, TiO_2 as a catalyst forms an electron hole, whereby holes are positively charged. When this hole is in contact with water molecules, it breaks down into *OH and H^+ ions. Electrons will react with dissolved oxygen and form O^{2-}, which then reacts with water molecules to produce OH^- and radical *OOH. The *OOH will combine with H^+ ions to form *OH and OH^-, while hole oxidized OH^- to form *OH. Hydroxyl radicals are radicals that attack the contaminants that are present in aqueous solution.[10]

Most previous studies on the photocatalysis of TiO_2 used a 1-dimensional (1-D) coating on a surface. However, dimension becomes a crucial factor in determining the properties of nanomaterials including surface area.[11] The interest of Electrospinning (ES) in fabricating ceramic nanofibers has grown exponentially since 2002.[12] and recently, it has become a popular technique to produce 2-D composite materials. This technology uses electric field to convert polymer solution (matrix) or melt it into a fiber form. The principle of ES is a syringe loaded with a polymer solution that is pumped at a constant flow rate. A specific voltage applied will induce an electric field between the needle tip and the collector. The solution will be charged, and the charge will accumulate at the surface of the liquid. As the voltage increases, the electrostatic repulsion of the solution will increase. The liquid is retained by surface tension. When the electrostatic repulsion is higher than the surface tension, a liquid meniscus with a conical shape is formed at the tip of the needle. The electric field and surface tension of the solution interact with each other, leading to stretching in the solution jet, which allows fibers to be formed. The whipping motion of the jets leads to the evaporation of the solvent and solidifies the fiber.[13]

In general, the quality of the electrospun fibers depends on 3 processing parameters: the ES experiment setup (voltage supply, flow rate, needle size, and needle tip-to-collector distance), sol–gel parameters, and the selection of precursors. The viscosity of the ES solution depends on the molecular

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weight of the polymer and the concentration of the mixture (polymer, solvent, and precursor). The polymer concentration will determine the fiber diameter,[14] and the diameter increases with the increase of TiO_2 precursor solution.[15] The advantage of ES is that it can produce nanofibers with diameters ranging from 50 to 500 nm. These small-size fibers improved the photocatalytic performance of nanomaterials. By using the ES technique, the mechanical, biological, and kinetic properties of electrospun fibers are easily manipulated by altering the matrix composition and processing parameters.[16]

Commonly, the electrospinning method is combine with sol-gel technique to synthesize the nanoparticles. The usual precursor used for TiO_2 was titanium isopropoxide (TIP), the matrix used was polyvinylpyrrolidone (PVP) due to its high molecular weight (130,000 g/mol), and the solvent used to dissolve PVP was ethanol. The anatase phase of TiO_2 was obtained by calcination of the fibers.

In our study, we introduced a new method to produce fibers using ES by avoiding the sol–gel and calcination process. We used TiO_2 powder that was synthesized earlier via hydrothermal method, and it was calcined to obtain the anatase phase. These nanoparticles were then incorporated into polyvinyl alcohol (PVA) as the matrix.

Literature Review

The use of electrospun TiO_2 fibers has become an interest in various applications, such as energy storage, health-care, biotechnology, environmental engineering, defense, and security.[17] Specifically for environmental engineering applications, the nanofibers require high porosity meshes, microscale interstitial space, large high surface area-to-volume ratio, and flexibility of structures, and mechanical performance, which enable them to be an excellent material for membrane fabrication.[17,18] Nowadays, the use of electrospun TiO_2 has become an interest for various applications as the nanofibers have significantly improved photocatalytic performance due to the small fibers. This has led to quick charge transfer to the dynamics of electron–hole recombination on a large specific surface area of TiO_2 nanofibers.[19] Alves et al[20] reported that the photocatalytic activity of TIP/PVP electrospun fibers was reduced due to the increase of heating temperature during calcination that resulted in decrease in fraction of anatase phase and surface area of the fibers. The photo-oxidative decomposition of methylene blue (MB) was compared to TiO_2 powder Degussa P-25. Li et al[15] have developed the ES technique without combining with sol–gel by using tetrabutyltitanate as the precursor, PVP as the matrix, and ethanol as the solvent. Mesoporous TiO_2 nanofibers with anatase were successfully produced after calcination at 500°C. This PVP/TiO_2 showed that the photodegradation rate of rhodamine B in aqueous solution was 99% under UV light. Hong et al[21] reported the removal of 99% acetone and 90% of particulate with size larger than 200 nm under UV irradiation (254 nm) by a non-woven membrane of PVA/TiO_2 (Degussa P25) prepared using electrospinning. There are many previous studies report on the technique to enhance the photocatalysis of electrospun TiO_2 fiber. Jeun et al[22] use electron beam irradiation on (PAN)/TiO_2 electrospun fibers to show an increase of about 24% in the photodegradation of MB. Mishra et al[23] studied the PVP/TiO_2 electrospun nanofibers functionalized with silver (Ag) nanoparticles to enhance the electronic and catalytic properties of TiO_2. Photocatalytic reaction using methyl red under UV light showed that the PVP/TiO_2/Ag composite degraded 30% of methyl red compared to 24% degradation for pure TiO_2 in a span of 265 minutes.

MATERIAL AND METHODS

Titanium dioxide powder was synthesized using hydrothermal method and was sintered at high temperature to obtain the anatase phase. For preparing the electrospinning solution, the deionized water was used as dispersant, polyvinyl alcohol (PVA) as the media for the fibers, a surfactant to stabilize the nanoparticles in the solution, and MB dye for photodegradation experiment.

Experimental

The fabrication of PVA/TiO_2 fibers using the ES technique was reported in 2021.[24] In this study the fabrication methods for PVA/TiO_2 fibers are similar to the one reported in 2021. However, in the current study, we focus on the optimization of the fabrication parameters: the first parameter is to vary the amount of PVA from 10-16 wt% and the second parameter is sonication time which was altered from 1-4 hours. The ratio of the PVA : TiO_2 mixture was 4 : 1, and the TiO_2 : SDS mixture was 10 : 1. The morphology of the electrospun fibers was characterized using field emission scanning electron microscope (GeminiSEM 500, Carl Zeiss) and the titanium (Ti) element was determined using energy-dispersive x-ray (X-Max 80, Oxford Instrument). The anatase phase was determined using an x-ray diffractometer (X'Pert Pro, Panalytical). The electrospun fibers were then removed from the aluminum foil and immersed in MB dye solution for photodegradation

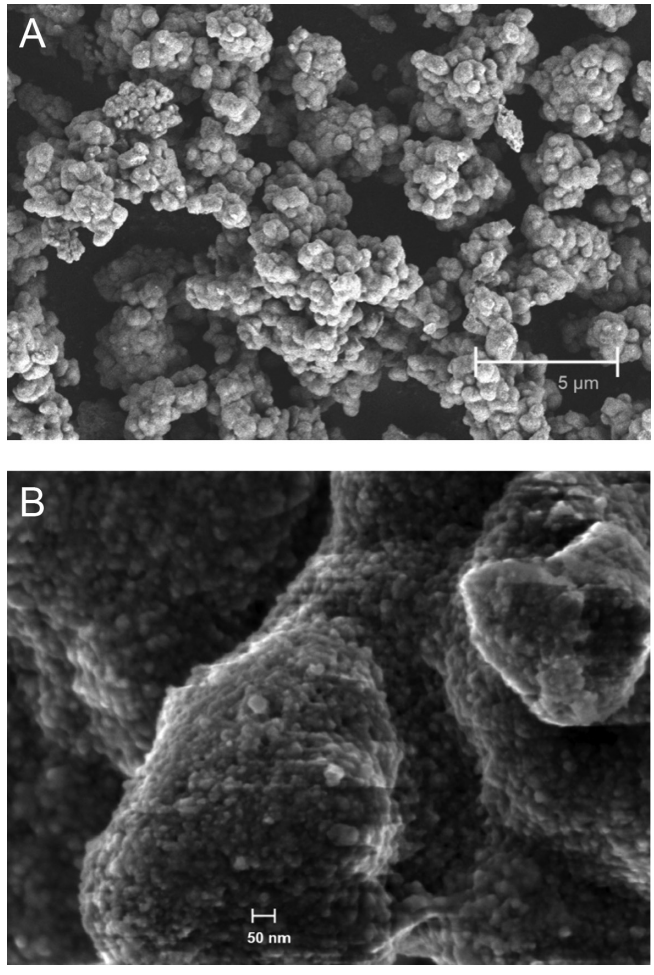

Figure 1. Electron images of titanium dioxide particles observed using field emission scanning electron microscopy at magnification of (A) 25 k×, and (B) 70 k×.

experiment using 400W UV light for 5 hours of exposure time. The degradation was determined based on the absorbance value at an interval of 1 hour obtained using a ultraviolet–visible spectrometer (Lambda 35, Perkin Elmer).

RESULTS AND DISCUSSION

The TiO_2 powder used in this study was characterized earlier using field emission scanning electron microscopy and x-ray diffraction analysis (XRD). Figure 1 shows the electron images for TiO_2 particles at 2 different magnifications. It was observed that at 25 kx magnification, the particles are heavily agglomerated. However, at 75 kx, the particles were observed as spherical and homogeneous, and the size was able to be determined at less than 50 nm.

The TiO_2 powder used in this study was characterized using XRD analysis. Figure 2A shows that the peaks are identified at $2\theta = 25.8°$, 38.15°, 48.53°, and 55.13°, which are identified as the anatase phase (ICSD: 01-070-6826). The differences between XRD spectra were compared to characterize the crystalline structure of PVA and PVA/TiO_2 fibers, as shown in Figure 2B. It is found that there are 2 peaks that only appear on the PVA/TiO_2 spectrum at $2\theta = 17°$ and 19°, indicating that the crystallinity of PVA fibers was affected by the presence of TiO_2 nanoparticles. The same results were also reported previously by Khan et al.[25] The broad peak at $2\theta = 25.8°$ is only observed on the pristine PVA fibers, which indicates that texturization occurred during the electrospinning process.[26] Texturization is a mechanism by which PVA changes its crystal structure to a preferred orientation to accommodate the presence of TiO_2 and surfactant during the electrospinning process.[27]

The XRD spectrum for PVA/TiO_2 fibers was further refined to determine the association of TiO_2 with the fiber, as shown in Figure 2C. It confirms that TiO_2 was associated with the fibers at $2\theta = 9.33°$, 13.23°, 17.16°, 19.31°, 21.86°, 24.51°, and 25.69°. These peaks are defined as anatase TiO_2 (ICSD: 98-009-4635). Furthermore, the degree of crystallinity determined by the under-the-curve measurement shows that PVA/TiO_2 fiber has a higher crystallinity (75.21%) compared to pristine PVA fiber (27.7%). The

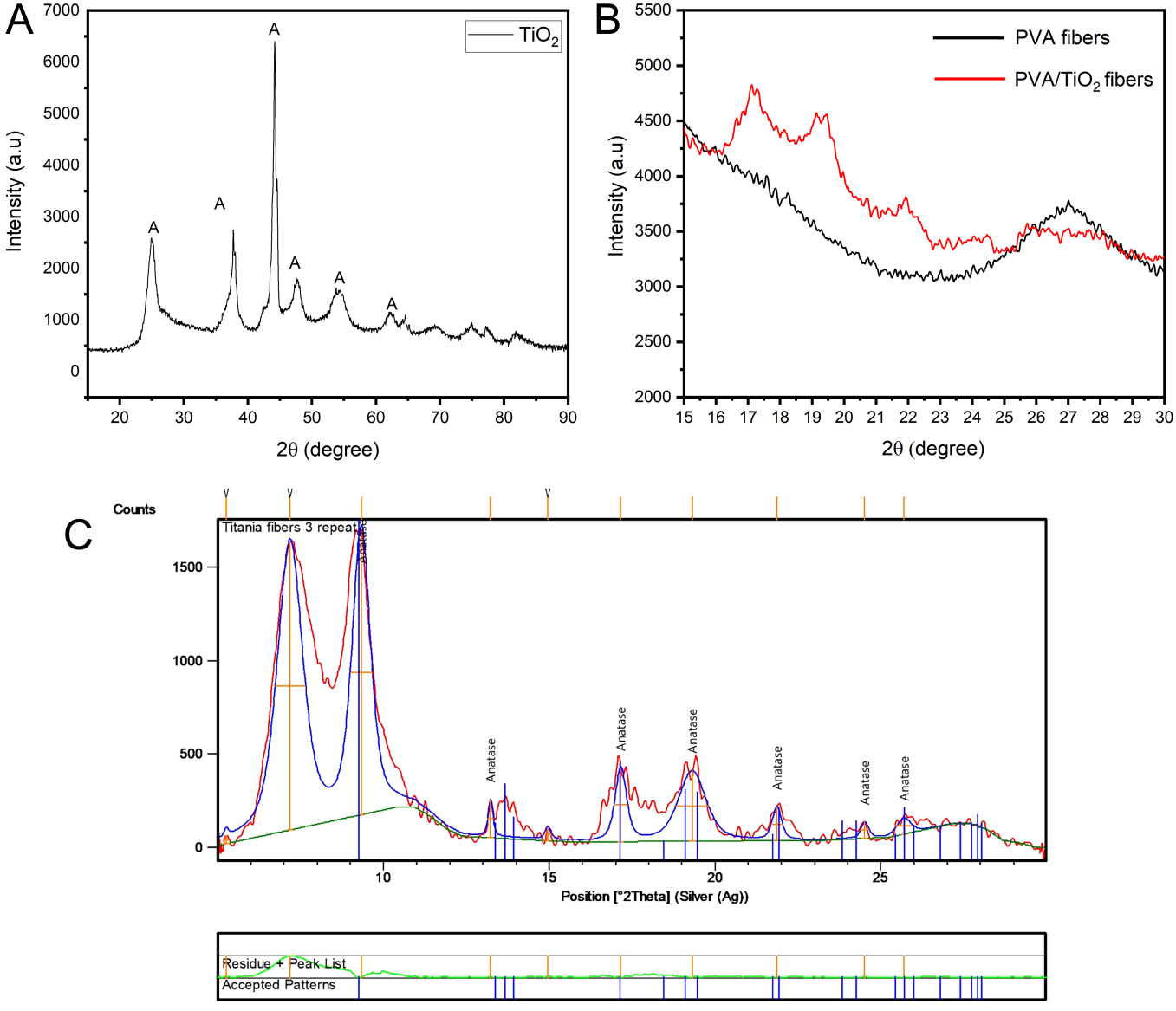

Figure 2. X-ray diffraction analysis spectra of (A) titanium dioxide (TiO_2) powder, (B) pristine polyvinyl alcohol (PVA) and PVA/TiO_2 fibers, and (C) PVA/TiO_2 fibers indicate refined peaks for anatase identification and area under curve measurement for degree of crystallinity.

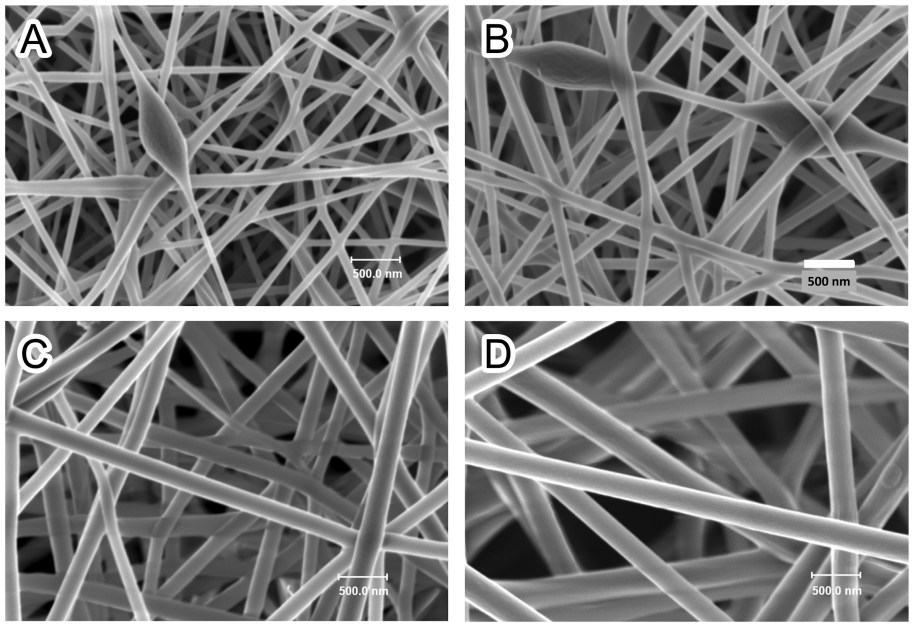

Figure 3. Electron images of polyvinyl alcohol (PVA)/titanium dioxide electrospun fibers with increasing PVA loading from (A) 10 wt%, (B) 12 wt%, (C) 14 wt%, and (D) 16 wt% observed at 25 k× magnification.

incorporation of TiO_2 into PVA interfered with the polymer chain through the steric effect and hydrogen bonding between PVA and TiO_2 nanoparticles (NPs). The hydroxyl group became more terminally extended, which made the crystalline structure rigid, resulting in reduced crystallinity of the pristine PVA fiber.[28]

Table 1. The Diameter of Polyvinyl Alcohol/Titanium Dioxide Fibers as a Function of Sonication Time

Sonication Time (hours)	Fiber Diameter (nm)
1	222
2	228
3	393
4	795

Figure 3 shows the electron images of PVA/TiO_2 fibers with different amount of PVA added. It is observed that as the wt% of PVA increases from 10 to 16 wt%, the fiber diameter also increases, and the spherical shape beads were formed at low wt%. This is related to the viscosity of the polymer solution. This is supported by the previous studies which showed the number of beads decreases as the viscosity increased.[29]

The fiber diameter of fibers prepared at 16 wt% in Figure 3 was measured and found that the size increases with sonication time.

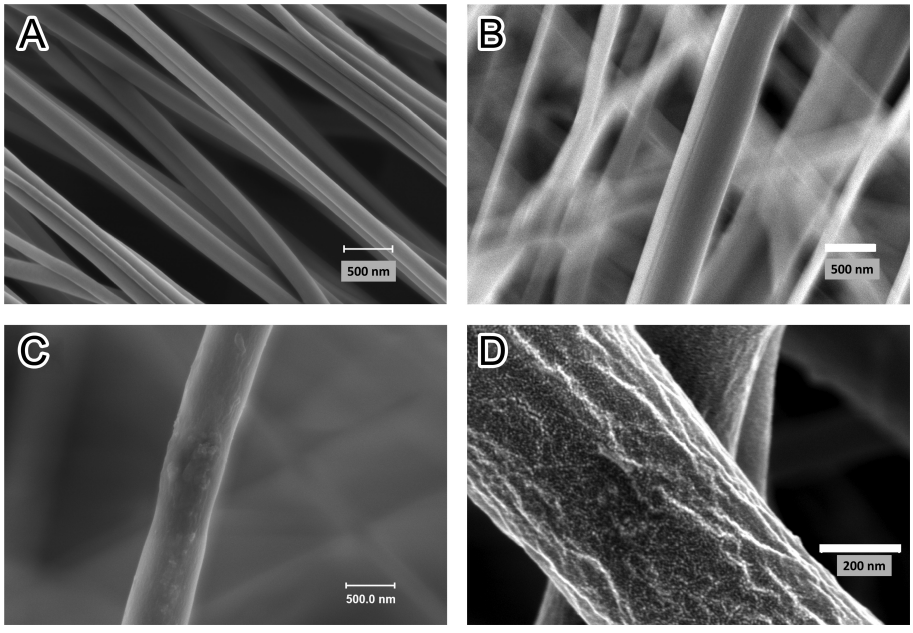

Figure 4. Electron images of fibers prepared at different sonication time; (A) pristine polyvinyl alcohol (PVA) fibers sonicated for 2 hours; (B) PVA/titanium dioxide (TiO_2) fibers sonicated for 2 hours; (C) PVA/TiO_2 fibers sonicated for 4 hours; and (D) PVA/TiO_2 fibers sonicated for 4 hours and magnified at 100 k×X. Magnification for (A)-(C) is 25 k×.

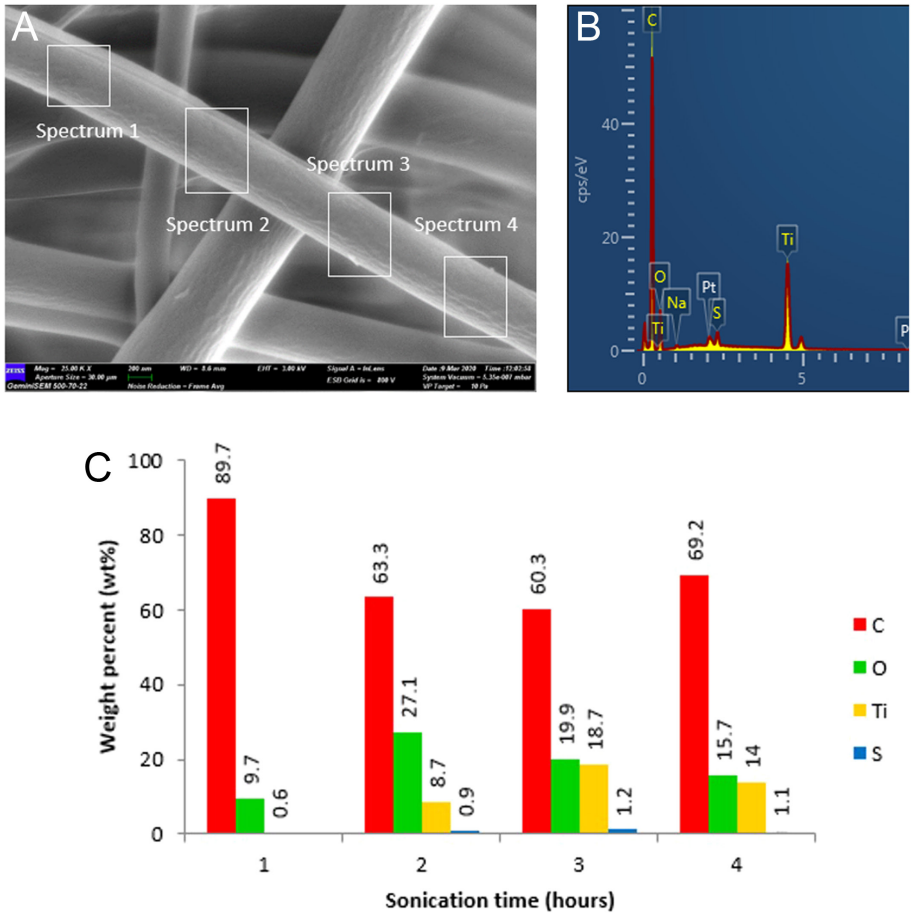

Figure 5. The field emission scanning electron microscopy/energy dispersive X-ray (EDX) elemental analysis of (A) 4 different spots on the polyvinyl alcohol/titanium dioxide fibers to detect the presence of titanium (Ti). (B) EDX spectrum indicates the presence of Ti and (C) the concentration of Ti (wt%) at different sonication times. C, carbon; O, oxygen; S, sulfur.

The diameter increases from 222 nm when sonicated at 1 hour and increases to 795 nm after 4 hours as shown in Table 1.

Sonication time is important to reduce the particle size of titania aggregates as smaller aggregates promote better incorporation of titania particles with PVA and thus form fibers with a larger diameter. Figure 4 shows that fibers produced with 4 hours of sonication time have a rougher surface, attributed to the titania aggregates appearing on the surface of the fibers as compared to fibers produced with 2 hours of sonication time and PVA-pristine fibers. The distribution of TiO_2 particles on the fibers' surface can be seen clearly at a magnification of 100 k×.

Figure 5A shows the FESEM/EDX elemental analysis measured at 4 different spots on the PVA/TiO_2 fibers' surface. Figure 5B shows the presence of titanium (Ti) element besides carbon (C), oxygen (O), and sulfur (S). The existence of Ti and O on the fibers' surface confirmed that TiO_2 nanoparticles are distributed on the fiber surfaces, while sulfur is attributed to the surfactant. The concentration (wt%) of Ti was measured as a function of different sonication times. It is found that the wt% of Ti increases with the increasing sonication time, as shown in the graph in Figure 5C.

The distribution of TiO_2 on the fiber is crucial, as it can affect the efficiency of the catalyst when used in wastewater treatment application. To study the catalysis effect of PVA/TiO_2 fibers, photodegradation is calculated from the UV-Vis absorbance measurement. The percentage of MB degraded in the solution is 60.5% for pristine PVA fibers and 75.7% for PVA/TiO_2 fibers. The rate of photodegradation is calculated as 0.081/min and 0.127/min for pristine PVA and PVA/TiO_2 fibers, respectively.

The fabrication process of PVA/ TiO_2 fibers using the ES method was successfully developed. The amount of PVA required to give the best fibers with the least numbers of beads was 16 wt%. The appropriate sonication time, which led to a homogenous distribution of TiO_2 particles on the fibers' surface, was 4 hours. X-ray diffraction confirmed the existence of Ti on the polymer fiber surface. This study proved that the PVA/TiO_2 fibers were able to degrade MB under UV exposure, and the presence of anatase TiO_2 loaded onto the fibers had increased the photodegradation rate.

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