Research Article

Photocatalytic Performance of TiO_2 Nanofibers as a Function of Fiber Diameter Using TiCl_4 as a Precursor

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We focus on the production of TiO_2 nanofibers with controllable diameters using a facile electrospinning technique at room temperature. The resulting nanofibers were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and ultraviolet-visible spectroscopy (UV-Vis). The most important electrospinning parameters including potential difference (kV), flow rate (mL/h), and the separation distance between electrodes (cm) were found to have significant influence on the diameter of the produced nanofibers. The photocatalytic performance of TiO_2 nanofibers was successfully demonstrated for decolorization of Rhodamine B (Rh.B) under UV light irradiation. It was found that fiber diameter has a crucial influence on the photocatalytic performance of TiO_2 nanofibers.

1. Introduction

Among several oxide semiconductors, titanium dioxide has a more helpful role in our environmental purification due to its nontoxicity, photocatalytic activity, photoinduced superhydrophilicity, selfcleaning, and antifogging effect [1, 2]. Many researches on titanium dioxide are going on since Fujishima and Honda discovered the photocatalytic activity of titanium dioxide in 1969 [3]. They found out that titanium dioxide decomposes water to hydrogen and oxygen by photoillumination. In this regard, much attention has been drawn towards their photocatalytic properties because of its application in environmental purification and decomposition of toxic and organic compounds into environmentally harmless components [4]. A key requirement for improving the photocatalytic activity is to increase the specific surface area and enhance the crystallinity [5]. Therefore, significant progress has been achieved in the development of one-dimensional (1D) nanomaterials such as nanofibers due to their intrinsically high porosities and large surface areas [6–10].

Among the most successful methods for producing nanofibers such as chemical reduction, layer-by-layer

self-assembly, and template-based techniques, electrospinning has attracted much attention since it is one of the most simple, versatile, and low-cost methods for generating nanofibers from a wide range of materials including polymers, composites, ceramics, and semiconductors [7, 11–14]. It provides the ability to produce long continuous fibers with typical diameters ranging from 50 nm up to few micrometers and length of up to several centimeters [15, 16].

In this work, we have prepared TiO_2 nanofibers by electrospinning technique using TiCl_4 as a precursor and studied the effect of electrospinning parameters such as applied electric field, distance between nozzle and collector and flow rate on structure, morphology and fiber diameter. We have also evaluated the diameter dependency of electrospun TiO_2 nanofiber on photocatalytic performance. In the majority of published papers, at least 5 to 6 precursors are used for preparation of primary sol, but in this method we have just used TiCl_4 and ethanol for formation of TiO_2 and also PVP as an appropriate polymer. To the best of author knowledge there were no published report, on electrospun TiO_2 fibers using TiCl_4 and ethanol which is a rather fast and one-step approach.

FIGURE 1: XRD pattern of dried at 100°C and heat-treated TiO₂ nanofibers at 550°C for 2 hours.

2. Materials and Methods

2.1. Synthesis of TiO₂ Nanofibers. The experimental setup of synthesis process which was arranged vertically, consists of a homemade DC high-voltage power source (30 kV, 5 mA), a double-syringe pump (Ascor AP 22), positive and negative electrodes, grounded conductive collector, and 20 mL syringes with syringe needles. The electrospinning was conducted in an open environment at the room temperature of approximately 25°C. An aluminum plate covered with aluminum foil was used as the collector screen and connected to the negative pole while positive pole was connected to the syringe needle. For preparation of electrospinning solution, 0.45 g PVP (Mw = 1300000) was dissolved in 10 mL ethanol (Merck, 99.8%). 1 mL TiCl₄ (Merck, 99%) was slowly added dropwise to the previous solution under vigorous stirring at room temperature and stirred for another 30 min at room temperature to get a homogenous solution. The final solution was then loaded into the syringe pump for electrospinning. In this work, a 2.5 to 15 kV voltage was applied in the distance range of 5 to 15 cm and flow rate of 0.3 to 10 mL/h. The as-spun nanofibers were dried at 100°C for 1 hour and then heat treated at 550°C for 1 h in order to remove PVP and crystallize TiO₂.

2.2. Characterization. Analysis of the crystalline structures was performed by XRD diffractometer (X'pert Philips) with wavelength of Cu K α radiation in 2 θ range from 20° to 80° by 0.04° sec⁻¹ steps. UV-Vis spectroscopy of the samples was taken out by a Lambda 950 spectrophotometer (Perkin Elmer) from 200 nm to 1100 nm wavelengths. SEM analysis was taken out by a SEM instrument (Philips XL30) at 5–20 keV accelerating energy, and TEM analysis was performed by a LEO 912 AB instrument at 200 keV accelerating energy by deposition of TiO₂ nanofibers onto the copper grid at room temperature.

2.3. Photocatalytic Study. Photocatalytic activity of the nanofibers was measured by photodegradation of (Rh.B), with the initial concentration and volume of 10⁻⁵ M and 30 mL, respectively, at the presence of 30 mL 0.01 wt% TiO₂ nanofibers. Actually 0.01 g of final residue which was a white fibrous substance of TiO₂ nanofibers dispersed in DI water to obtain a 0.01 wt% nanofibrous TiO₂ solution. Then, the mixed (Rh.B) and TiO₂ solution was stirred in dark for 30 min to equilibrate the adsorption/desorption between dye molecules and TiO₂ photocatalysts. Then, it was irradiated at room temperature by a 15 W low-pressure mercury lamp, 254 nm strongest peak wavelength. The degradation rate was measured by UV-Vis spectrophotometer at the maximum absorption wavelength of (Rh.B).

3. Results and Discussion

3.1. Crystal Structure. XRD analysis was taken out to find the crystalline phase and structure of the produced structures. The results for dried and heat-treated sample is depicted in Figure 1. As it is clear from the XRD pattern, the dried fibers at 100°C are amorphous and heating them at 550°C for 1 hour leads to formation of a white residue which is the crystalline TiO₂ nanofibers in anatase phase. The obtained spectrum after heat treatment at 550°C in air for 1 hour has the TiO₂ anatase phase peaks at 2 θ = 25.3, 37.7, 47.8, 54, 62.7, 68.6, 70.3, and 75.2 degrees with no impurity which is in agreement with 21-1272 standard cards from JCPDS. Heating the as-spun TiO₂ nanofibers results in PVP removing and crystallization of TiO₂. These results are in good agreement with previous reports [6, 10].

3.2. Microscopic Study. Applied electric field is the most important parameter in the electrospinning process due to its direct impact on the dynamics of the fluid flow and as a result the structure and morphology of produced fibers. The

FIGURE 2: SEM images and the corresponding measured average fiber diameter of TiO_2 nanofibers synthesized at a fixed 5 cm distance and (a) 2.5 kV, (b) 5 kV, (c) 7.5 kV, and (d) 10 kV potential difference (the white scale bars in all SEM images are 1 μm).

FIGURE 3: SEM images of final products prepared at lower than threshold. (a) electric field, (b) flow rate, and (c) typical TEM image of TiO₂ nanofiber prepared at 5 cm distance and 5 kV potential difference.

changes in the applied voltage will be reflected on the shape of the pendant droplet at the needle tip, its surface charge, dripping rate, velocity of the flowing fluid, and hence on the fiber structure and morphology [17]. Figures 2(a)–2(d) show SEM images of TiO₂ nanofibers synthesized at a fixed 5 cm distance and different electric fields. As is clear from SEM images, the mean diameter of fibers decreases by increasing applied voltage (scale bars in all SEM images are 1 μ m). The applied voltage imposed an electrical polarization stress on the fluid drop at the needle tip and causes the elongation of the droplet. As the charged droplet ejects from the needle tip, it accelerates toward the collector and during this process the charged fluid encounters bending instability due to columbic repulsion between charged sections within the fluid jet. This bending instability is responsible for the stretching of the strands as they change from liquid into a solid form. Consequently, an inverse relationship exists between the diameter of the nanofibers and the applied voltage between the electrodes, and by increasing potential difference, the fiber diameter decreases [17]. By more increase of the applied voltage in a fixed 5 cm distance, a visible arc happens between the needle and collector. The minimum fiber diameter was found about 80 ± 16.6 nm which was obtained at 10 kV. Table 1 summarizes all the experiments and the resulting calculated average fiber diameter. Fibers were not formed at potential differences lower than 2.5 kV and also flow rates lower than 0.3 mL/h in a fixed 5 cm separation distance (see Figures 3(a) and 3(b)). Figure 3(c) shows the typical TEM image of TiO₂ nanofibers at 5 cm distance and 5 kV applied voltage.

TABLE 1: Summary of experimental conditions.

No.	Applied voltage (kV)	Separation distance (cm)	Flow rate (mL/h)	Average fiber diameter (nm)
1	2.5	5	0.3	220 ± 43.6
2	5	5	0.3	140 ± 21.4
3	7.5	5	0.3	110 ± 18.3
4	10	5	0.3	80 ± 16.6
5	10	10	0.3	60 ± 8.2
6	10	15	0.3	40 ± 6.3
7	10	5	1	100 ± 17.6
8	10	5	3	120 ± 20.8
9	10	5	10	160 ± 27.6

Similarly, the needle tip to collector distance is also a major factor in determining the fiber diameter. The effects of varying voltage and needle collector distance were studied individually by keeping other parameters constant. Figure 4 illustrates SEM images of TiO₂ nanofibers prepared at a fixed 10 kV applied voltage and different needle tip to collector distances. By increasing distance in a constant electric field, the average fiber diameter decreases. Increasing the separation distance between the needle and collector results in longer pass time for the charged fluid jet ejected from the needle. Therefore, as the distance increases, the fibers tend to become more elongated and smaller in diameter. Thus,

FIGURE 4: SEM images and the corresponding measured average fiber diameter of TiO₂ nanofibers prepared at a fixed 10 kV applied voltage and (a) 10 cm and (b) 15 cm separation distance.

an inverse relationship was observed between the separation distance and the TiO₂ nanofiber diameter. Accordingly, smaller diameter nanofibers were produced as the separation distance increased [17].

SEM images of TiO₂ nanofibers prepared in fixed 5 cm distance, 10 kV applied voltage, and different flow rates are demonstrated in Figure 5. It is clear from SEM images that by increasing the flow rate from 0.3 mL/h to 10 mL/h and keeping the potential difference and separation distance constant, the mean fiber diameter increases. In fact, increasing the mass throughput at the needle tip in a fixed electrical field and separation distance results in a higher rate of TiO₂ deposition onto the collector surface. Thus, nanofibers with bigger diameters were formed as the flow rate increases.

Recently, Ray and Lalman [17] both theoretically and experimentally showed that three preliminary experimental factors including potential difference, flow rate, and separation distance have crucial effect on the fiber diameter. They have found that by increasing the applied voltage and

separation distance the mean fiber diameter decreases, which is in close agreement with our results.

3.3. Photocatalytic Activity Measurements. Changes in the absorption spectrum of Rh.B as a standard dye under UV illumination at different irradiation times for TiO₂ nanofibers prepared at different experimental conditions and one Rh.B sample as reference are illustrated in Figure 6. No remarkable changes in the concentration of the Rh.B solution were observed in the absence of TiO₂ nanofibers. Therefore, decomposition of Rh.B only depends on the photoexcitation of TiO₂ nanofibers. It was observed that by increasing the irradiation time the maximum absorption peak decreases. This indicates that the concentration of Rh.B is decreasing at the presence of TiO₂ nanofibers and UV light illumination. Figures 6(a)–6(c) demonstrate the changes in concentration, of Rh.B as a function of time under UV irradiation for TiO₂ nanofibers with different diameters. C and C_0 are the reactant concentrations at time $t = t$ and $t = 0$, respectively. As is clear from the obtained results, the photocatalytic performance

FIGURE 5: SEM images and the corresponding measured average fiber diameter of TiO_2 nanofibers prepared in 5 cm distance, 10 kV applied voltage and (a) 1 mL/h, (b) 3 mL/h and (c) 10 mL/h flow rates.

is stronger in all smaller diameter fibers rather than larger-diameter fibers.

4. Conclusion

In summary, TiO_2 nanofibers were prepared using the simple, facile, and inexpensive electrospinning technique at room

temperature. Fiber diameter was successfully controlled by controlling the applied voltage, flow rate, and spinning distance. We have found that by increasing the potential difference and needle to collector distance the mean fiber diameter decreases. Also, we have observed that by increasing the flow rate and keeping the potential difference and separation distance constant the average fiber diameter increases.

FIGURE 6: Evaluation of photocatalytic activity of TiO₂ nanofibers prepared at (a) fixed 5 cm distance and different electric fields, (b) fixed 10 kV applied voltage and different separation distances, and (c) fixed 5 cm separation distance, 10 kV applied voltage and different flow rates by photodegradation of Rh.B. under UV light irradiation.

Photocatalytic performance of prepared TiO₂ nanofibers was measured by photodegradation of Rh.B under UV illumination as a model dye. It was found that photocatalytic activity of TiO₂ nanofibers depends on electrospinning parameters and consequently the fiber diameter.

Conflict of Interests

The authors confirm that they do not have any financial relation with the commercial identities mentioned in their paper.

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