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The Morphology of Electrospun Titanium Dioxide Nanofibers and Its Influencing Factors

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Abstract. Titanium dioxide (TiO_2) has high photocatalytic activity and it is extensively applied in solar cell technology and environmental science. Electrospinning is acknowledged as the most versatile technique to fabricate nanofibers such as metal oxide nanofibers. Titanium dioxide nanofibers are generally prepared by electrospinning organic solutions containing alkoxide precursors and a carrier polymer with high voltage supply. The paper discusses on electrospun TiO_2 nanofibers including the spin dopes preparation history, influencing factors on fiber morphology and fiber characterizations. In particular, the parameters such as spin dopes viscosity, supplied voltage, feeding rate and effect of temperature that affect the morphology of the nanofibers are emphasized. Based on several studies, smaller diameter of TiO_2 nanofibers can be produced with lower viscosity solution, higher voltage and lower feeding rate. The heat treatment of 500 ^{o}C reduced the fiber size and produces crystallized anatase TiO_2 nanofibers.

1 Introduction

Titanium dioxide (TiO_2) have attracted the interests and attentions of the researchers because it is low cost, environmental friendly and exceptional chemical stability with extraordinary optical and electronic properties [1-5]. TiO_2 nanofibers with wide band gap are promising material in the applications of photocatalysis, solar cell, optical filter and antimicrobial surface coating [5-7]. TiO_2 exists in both amorphous and crystalline forms, in which amorphous form is photocatalytically inactive. There are three crystalline TiO_2 phases, namely anatase, rutile and brookie. Of the phases, anatase and rutile are found to be suitable for photocatalytic applications where as brookie is not being tested for photocatalysis [8]. Anatase TiO_2 is metastable and exhibits high activities for solar cell applications due to its higher band gap (3.2 eV). On the other hand, rutile TiO2 is thermodynamically more stable, and due to the low intrinsic photocatalytic activity with lower band gap (3.0 eV), it can be applied in the cosmetic field and tissue engineering [9-12]. One dimensional nanoarchitectures TiO_2 offers faster electron transportation rate, high porosity and larger surface [13]. One dimensional nanostructures TiO_2 such as whiskers, rods, tubes, wires, belts, spirals and fibers have been produced by sol-gel synthesis, electrochemical fabrication, dip-coating, hydrothermal technique, electroless deposition, crystallize growing method and electrospinning [13-16]. To date, TiO_2 nanofibers are prepared by using crystallize growing method and electrospinning. Crystallize growing method takes

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extremely long growing time and does not produce uniform fibers [13]. Hence, electrospinning has engrossed the attention of the researchers.

Electrospinning appears as a novel, versatile, simple, cost effective and straightforward technique to produce fibers with diameters down to tens of nanometers, from various materials such as polymers, metal oxides and composites [11, 14, 16]. In a typical electrospinning system, there are three basic components to be used: a high voltage supply, a needle of small diameter with syringe that is connected to a syringe pump and a grounded metal collector [17]. The schematic diagram for a typical electrospinning set up can be referred to [18].

2 Chronology of Spin Dopes Formulation

The titanium dioxide-based spin dopes can be prepared from organic solutions containing alkoxide precursors and a carrier polymer [19]. The alkoxide precursors are titanium tetraisopropoxide (TTIP) or Titanium (IV) n-butoxide (TNBT), the carrier polymers are polyvinylpyrolidone (PVP) or polyvinyl acetate (PVAc). The solvent for the spin are ethanol, dimethyl formamide (DMF), methanol or isopropanol. Acetic acid is a popular choice of catalyst in the spin dopes preparation among many researchers. A summary of the spin dopes which have been productively electrospun into TiO_2 nanofibers by different researchers is presented in Table 1.

Table 1. Spin dopes to fabricate electrospun TiO2/PVP composite nanofibers.

No	Precursor	Carrier Polymer	Solvent	Catalyst	Fiber size (nm)	Ref.
1	Titanium (diisoproproxide) bis (2,4-pentanedionate) 75 wt.% in 2-propanol	PVP (Mw 1,300,000)	Ethanol	Acetic acid	132 ± 24	[7]
2	TNBT	PVP (Mw 1,300,000)	DMF	Acetic acid	50-500	[9]
			DMF/Isopropanol ratio 1/1			
			Isopropanol	Acetic acid	200-2000	
3	TTIP	PVP (Mw 1,300,000)	Ethanol	Acetic acid	200-800	[11]
4	TTIP	PVP	Ethanol	Acetic acid	100-200	[12]
5	TTIP	PVP (Mw 1,300,000)	Ethanol	Acetic acid	200-2000	[16]
6	TNBT	PVP (Mw 360,000)	DMF	Acetic acid	920-1800	[19]
7	TNBT	PVP (Mw 1,300,000)	Ethanol	Acetic acid	200-300	[20]
8	TTIP	PVP (Mw 1,300,000)	Ethanol	Acetic acid	20-200	[21]
9	TNBT	PVP (Mw 1,300,000)	Methanol	Acetyl acetone	150-200	[22]
10	TTIP	PVP (Mw 1,300,000)	Ethanol	Acetic acid	150-200	[23]
11	TTIP	PVAc (Mw 500,000)	DMF	Acetic acid	150-600	[24]
12	TTIP	PVP (Mw 1,300,000)	Ethanol	Acetic acid	70-150	[25]
13	TTIP	PVP (Mw 1,300,000)	Ethanol	Acetic acid	30-200	[26]
14	TTIP	PVP (Mw 300,000)	Ethanol	Acetic acid	184-343	[27]
15	TTIP	PVAc (Mw 800,000)	DMF	Acetic acid	200-600	[28]

Spin dopes consists of the combination of TTIP, PVP (M_w 1,300,000) and acetic acid in ethanol is the most commonly used to fabricate TiO_2 fiber.

In this paper, a systematic review is worked out on the electrospun TiO_2 nanofibers materials selections and parameters that affect the morphology of the nanofibers and the characterization of TiO_2 nanofibers. There are several factors that influence the morphology of the fibers such as applied voltage, flow rate, tip to collector distance and type of collector. However, this paper mainly discusses for the spin dope viscosity, supplied voltage and feeding rate.

3 Main Factors Influencing the Fibers Morphology

3.1 Spin dopes viscosity

The polymer concentration plays a significant role in determining the diameter of the nanofibers. The increase in polymer concentration may consequently elevates the viscosity of the spin dopes significantly [29]. Furthermore, the rise in alkoxide precursor (TTIP) may cause a slight increase in the spin dopes viscosity. In TiO_2 nanofiber fabrication, the increase of polymer concentration cause the expansion of fabricated fiber diameter [21]. Lee et al. [30] found that when the PVP concentration is increased from 0.04 g/ml to 0.10 ml, the fibers size increase significantly from 125 nm to 275 nm while the TTIP concentration raises from 0.12 g/ml to 0.18 g/ml results in increase of the fiber diameter from 200 nm to 280 nm. This has been proved later by [11] and [16]. Thus, the viscosity is greatly affected by the polymer concentration in the spin dopes. When the spin dopes viscosity is higher, under a fixed supplied voltage and feeding rate condition, the fiber formation initiation cannot take place due to the insufficient force to stretch the fibers to the thinner size [11]. At a higher concentration of TTIP, a higher supplied voltage is needed in order to initiate the fiber formation. In order to produce smaller diameter of TiO_2 fibers, it is suggested that the spin dopes should have a lower concentration of PVP in order to obtain smaller size of TiO_2/PVP composite fibers.

3.2 Supplied voltage

Bharwaj and Kundu [18] stated that the fibers can be formed provided the supplied voltage is at the threshold stage which subsequently induces the essential charges on the solution to initiate the electrospinning process. In the fabrication of TiO_2 nanofibers, the fibers' diameter can be reduced by raising the supplied voltage. Li and Xia [21] proved that the fibers size is abruptly decreased from 110 nm to 55 nm as the supplied voltage is raised from 5 kV to 20 kV. In addition, the mean diameter of the fabricated fibers decreases from 110 nm to 80 nm when the supplied voltage of 15 kV is increased to 25 kV [31]. Higher supplied voltage leads to a greater stretching on the spin dopes as the higher electrostatic repulsive force is formed and effectively reduce the fibers size. This causes rapid evaporation of the solvent, which contribute in the fiber size reduction [18]. However, discontinuity in nanofibers occurs when the supplied voltage exceeded 20 kV, causing the occurrence of over pulling effect with the fiber breakage [13, 31-32]. Thus, to fabricate a continuous smaller fibers, the supplied voltage should be within 15-20 kV. The optimized TiO_2 nanofibers can be generated with the supplied voltage of 18.4460 kV based on the morphology analysis [16].

3.3 Feeding rate

Feeding rate, which is tunable by the syringe pump, influences the jet velocity and the transfer rate. Faster feeding rate of spin dopes may result in wider size of fabricated TiO_2 fibers [21, 30]. The study by Jung et al. [13] showed that composite TiO_2/PVP fibers' mean diameter increased from 120 nm to 180 nm with the increment of flow rate from 0.1 mL/hr to 0.3 mL/hr. When the jet velocity is high, the volume ejected is greater and thus it caused the solution is electrospraying sequel of insufficient stretching under the constant supplied voltage [33]. High transfer rate of the jet solution cause the jet

to reach the collector rapidly without proper drying time and reflex in larger fibers formation [18]. Thus, the feeding rate should provide adequate time for the solvent to evaporate before reaching collector. Moreover, it is suggested that the optimized morphology of TiO_2 composite nanofibers can be obtained at 0.70 mL/hr [16].

3.4 Heat treatment

Heat treatment is needed after the spin dopes is electrospun on the collector. The electrospun TiO2/PVP composite nanofibers are heated up to 500°C to eliminate PVP and remaining solvent which can reduce the size of fibers [13]. Although calcined at a temperature of 200 °C is enough to eliminate the polymer and solvent, the fibers may stay in amorphous form. Thus, it is suggested that the TiO_2/PVP composite nanofibers is to be sintered up to 500°C to obtain pure TiO_2 nanofibers in crystallize form. However, for sintering more than 600°C, the fibers will transform from anatase to rutile phase [11, 13, 34]. A shrinkage of 35-70% of the diameter when the fibers is annealed at the temperature of 450-500 °C [13-14, 36].

In general, X-ray Diffraction (XRD) is used to determine whether the nanofibers are in amorphous or crystallize form. However, for crystallized TiO_2 nanofibers, XRD is used to identify whether the fibers are either in anatase or rutile phase. Figure 1 shows the heat treatment of TiO_2 nanofibers at different temperature, form and different phase of TiO_2. The nanofibers were converted from amorphous to crystallize form after annealing at 550°C; beyond 400°C, TiO_2 exhibits in anatase phase then at rutile phase when is calcined at 700°C.

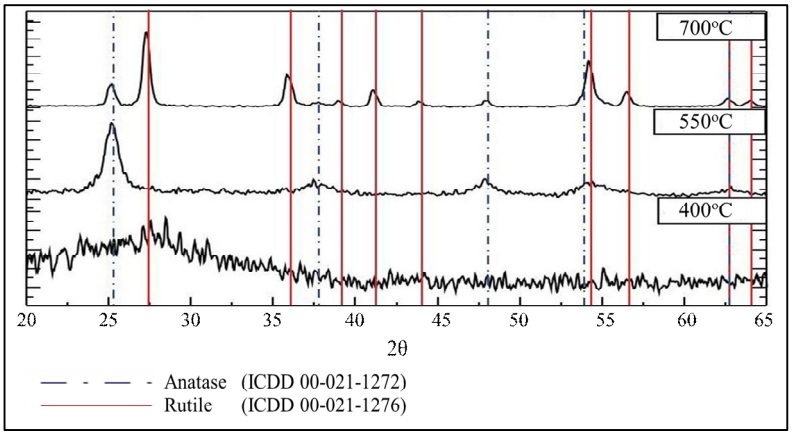

Figure 1. XRD analysis for TiO_2 nanofibers at different temperature of heat treament. TiO_2 is in amorphous form at heat treatment below 400 °C; showing crystallize form at higher temperature with 500°C showing anatase phase and 700 °C showing rutile phase [11].

4 Fibers Characterizations

4.1 Morphology analysis

The morphology of the fabricated composite nanofibers can be revealed by using scanning electron microscope (SEM). The micrograph of SEM provides the diameter of the fibers and the surface condition of the fibers. The diameter of the generated nanofibers as presented in Table 1 was determined and observed by using SEM. The electrospun TiO2/PVP composite nanofiber is straight with smooth surface without heat treatment. The TiO2 fiber is found to have rough surface due to crystallization of TiO_2 when it is calcined. When the fiber is sintered to 700°C and above, the surface structure shows some burl and to have nanocrytallize structure. This is because when the calcination

temperature increases, the crystallize growth of the TiO_2 fibers is better [5]. This is further done by [11, 13, 34-35]. The surface structure of the fibers is clearly shown with lower accelerating voltage (e.g. 5-10 kV) of SEM can provide the clearer surface structure image. Meanwhile, in order to measure the diameter of the fiber, the magnification should be range 10k to 200k [11, 16, 35].

5 Conclusions

TiO_2 nanofibers can be produced by using electrospinning process. The diameter of the nanofibers is tunable by changing the parameters especially the applied voltage, feeding rate and PVP concentration. An optimized fiber was suggested to produce at 18 kV, 0.7 mL/hr with 6.5% PVP concentration. Based on the desired applications, the TiO2 nanofibers may transformed from amorphous to crystallize form at 450-500^{o}C. It can be converted from anatase to rutile by calcination of 700 ^{o}C and above.

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