PHOTOACTIVE POLYACRYLONITRILE FIBERS COATED BY NANO-SIZED TITANIUM DIOXIDE: SYNTHESIS, CHARACTERIZATION, THERMAL INVESTIGATION

HADI FALLAH MOAFI, ABDOLLAH FALLAH SHOJAIE* AND MOHAMMAD ALI ZANJANCHI

Department of Chemistry, Faculty of Science, University of Guilan, P.O.Box 1914, Rasht, Iran

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ABSTRACT

Anatase nanocrystals were successfully synthesized and deposited onto polyacrylonitrile fibers with photocatalytic self-cleaning activity using the sol-gel process at low temperature. The original and treated samples have been characterized by several techniques such as scanning electron microscopy, fourier transform infrared spectroscopy, x-ray diffraction, diffuse reflectance spectroscopy, thermogravimetric analysis and differential scanning calorimetry. The TiO_2 nanoparticles, have been found to form a homogeneous thin film on the fiber surface. The photocatalytic activity, tested by measuring the degradation of adsorbed Eosin Yellowish dye. The photoactivity of the titanium dioxide coated fibres is much higher than that observed in case of untreated fibers. The photocatalytic self-cleaning properties of the treated fibers was fully maintained performing several cycles of photodegradation. This preparation technique can be also applied to new fabrics to create self-cleaning properties in them. The thermogravimetric study of PAN/ TiO_2 composite showed a slight increase of weight loss in the second step, which implied that, the dehydrogenation and oxygen uptake reactions would be promoted by the TiO_2 to some extent.

Keywords: Polyacrylonitrile; Titanium dioxide; Thermogravimetric analysis; Differential scanning calorimetry; Photodegradation; Eosin Yellowish

1. INTRODUCTION

Polyacrylonitrile (PAN) is one of the most widely used precursor polymers for making high performance carbon fibers [1–5]. Study of the degradation of polyacrylonitrile has been a subject of interest for decades owing to its commercial value for the production of carbon fibers [6–10]. Spectroscopy, including infrared, ultraviolet, solid-state nuclear magnetic resonance (NMR) and x-ray photoelectron spectroscopy (XPS), and thermal analysis, including differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetric analysis (TGA), are the common tools in the study of polyacrylonitrile degradation [11–14].

Semiconductor photocatalysis has been gathering much attention recently due to its promising application in chemical conversion and storage of solar energy for solar cells, hydrogen production, refractory pollutants elimination and self-cleaning surface [15–18].

Among various oxide semiconductor photocatalysts, titanium oxide (TiO_2) has been proven so far to be the most promising material used for both fundamental research and practical applications. Because of its highly efficient photoreactivity, biological and chemical inertness, cost effectiveness, non-toxicity, and long-term stability against photocorrosion and chemical corrosion, titanium dioxide has been frequently employed in the environmental treatment and purification purposes [18–22]. Anatase TiO_2 has been identified as the most effective and useful photocatalyst under near UV illumination [23].

The pairs of free electrons and holes are formed in the conduction and valence band region of TiO_2 under the UV irradiation, which react with oxygen and adsorbed hydroxyl group to produce superoxide ($\cdot\text{O}_2^-$) and hydroxyl radicals ($\cdot\text{OH}$) [18]. These highly reactive oxygen species possess strong oxidation potential to decompose a variety of calcitrant organic pollutants and kill pathogenic microorganisms [24].

Self-cleaning treatment technology of fibers by incorporation of titanium dioxide nanoparticles is a new concept that has been introduced in recent years [25,26]. With the

fast-growing demand towards functional fibers, where fibers not only have the basic characteristics such as maintaining thermal insulation, air permeability and elasticity, but also possessing extra functionality such as self-cleaning, anti-bacterial, environmental friendly, and anti-pollution [27–40]. It is anticipated that self-cleaning fibrous materials would have significant potential in the global commercial market. Therefore, this novel concept continues to open up exciting opportunities for further research and development.

The aim of this study is to develop a simple and repeatable anchoring procedure of the TiO_2 nanophase onto the polyacrylonitrile fibers. The photocatalytic self-cleaning abilities of our prepared fibers were investigated by studying the solid-phase photodegradation of the dye which is pre-adsorbed onto the TiO_2 -modified fibers. Also the thermal properties of pure and TiO_2 coated polyacrylonitrile fibers were investigated in air and nitrogen atmosphere.

2. EXPERIMENTAL

2.1. Materials

Polyacrylonitrile fiber (PANF), is a commercial product containing polyacrylonitrile and vinyl acetate with a diameter of about 20 μm . The other chemicals used in the study were of reagent grade. All chemicals were from Merck Company. De-ionized water was used in all the experiments.

2.2. Synthesis procedure

The fiber samples were treated with acetone for 60 min to remove impurities and dried at room temperature for 12 h. Titanium isopropoxide (TIP) was used as a precursor of TiO_2 . A solution was prepared as follows: Titanium isopropoxide (0.01 mol) was added to 2-isopropanol (50 mL) under vigorous stirring conditions and then triethylamine (0.005 mol) was added as a stabilizer of the solution and stirred (200 rpm) for 15 min under an inert environment. The required inert environment was made by argon gas flow through the system. A second solution was then prepared separately as follows: hydrochloric acid (1 mL) and water (0.5 mL) were added to 2-isopropanol (50 mL) and mixed well by a magnetic stirrer for 10 min. The two solutions were then mixed together and stirred vigorously for 60 min under argon gas flow. The formed TiO_2 sol was transparent and quite stable

For the impregnation, the PAN fibers after being dried in a preheated oven are then immersed for 5 min in the TiO_2 containing liquid sol. The extracted samples were then placed in 70 °C preheated oven to remove the solvent from the fiber and then heated at 200 °C for 10 min, to complete the formation of titanium dioxide from the precursor. Finally, the impregnated fibers were treated in de-ionized water. During this step the unattached TiO_2 particles were removed from the fiber surface.

2.3. Photocatalytic test

The photoactivity of the titanium dioxide coated PAN fibers has been investigated by exposing the samples containing adsorbed Eosin Y (EY) to UV-Vis light. For this purpose, aqueous solution ($1.0 \times 10^{-3} \text{M}$) of Eosin yellowish (EY) was prepared. Both bare and TiO_2 -covered fibers were treated in EY solution. The same amount of each sample was immersed under mild stirring in the same amount of the solution and remained overnight to complete the adsorption. The fibers were drawn out of the dyes solution and dried at room temperature. Subsequently, the so-obtained samples were exposed to UV-Vis, testing their photoactivity.

2.4 Characterization techniques

To investigate the morphology of the pure and TiO₂-modified PAN fibers, SEM (scanning electron microscopy) images were obtained on a SEM instrument (Philips, XL30) equipped with energy dispersive spectroscopic (EDS) microanalysis system to compositional analysis of the TiO₂-coated polyacrylonitrile fibers. To analyze the PAN polymer chain quality before and after the treatment FTIR analysis was performed on the samples mixed with KBr. The spectra were recorded with a Vertex70, Bruker spectrometer. X-ray diffraction measurements were performed on a Philips PW1840 diffractometer with Cu- K α radiation, scan rate 0.02 2 θ /s and within a range of 2 θ of 10 to 80 at room temperature. For photodecomposition reaction, the UV-Vis reflectance spectra were recorded at room temperature by a UV-2100 Shimadzu Spectrophotometer in the reflectance mode by investigating the evolution of the absorbance. For photocatalytic reactions, the irradiation was carried out on dry sample, by means of a high-pressure mercury lamp (HPMV 400W, Germany). The lamp yields a spectrum ranging from ultraviolet to visible radiation (200-800 nm). To investigate the quantity of TiO₂-deposited film and thermal behavior of samples, thermogravimetric analysis was performed in air flow (ramp of 10 °C/min) by Thermogravimetric analyzer (TGA V5.1A DuPont 2000). Differential scanning calorimetry (DSC) experiments were carried out on a Rheometric Scientific STA-625 instrument. Samples were heated up to 500 °C under nitrogen atmosphere at a heating rate of 10 °C/min.

3. Results and discussion

3.1. SEM and EDS analysis of TiO₂ coatings

In order to investigate the morphology of the obtained samples, comparison between the SEM images of the treated and untreated PAN fibers is illustrated in Figure 1. In the Figure 1a, on the surface of fiber, folds are evident. Figure 1b clearly shows that treated fibres are covered by a continuous and homogeneous TiO₂ thin film. SEM study of TiO₂ thin film deposited on polyacrylonitrile fibers, indicate that the particle size of the deposited titania on the fibres surface are less than 50 nm (Figure 1b). Rare and large TiO₂ nanocrystals aggregates, emerging from the fiber coating, are identifiable.

Figure 1: SEM images of: (a) pure fiber, (b) TiO₂-coated fiber, (c-d) enlarged TiO₂-coated fibers.

In Figure 2 the EDS analysis of TiO₂-covered fibres after washing are reported. On the basis of this result, it is noteworthy to observe that the deposited material consists of titanium and oxygen and after washing, remarkable amount of titania is still present on the PAN surface. This means that TiO₂ particles are firmly anchored to the surface of fibres. The continuous and homogeneous nature of the TiO₂ films suggests that pollutant molecules impinging the fiber-TiO₂ composite will interest preferentially with the TiO₂ phase covering the fibres.

Figure 2: EDS spectra of: TiO₂-coated PAN fiber after washing.

3.2. X-ray diffraction (XRD) analysis

The XRD patterns of pure and titania-coated PAN are reported in Figure 3. Figure 3a reports two broad peaks and one intense peak at 17° and 29°, respectively, which constitute the typical XRD pattern of PAN fibers [41]. Figure 3b shows XRD pattern of TiO₂-covered fibres. Since the amount of TiO₂ was low as determined by elemental analysis TiO₂ did not show a crystalline phase. This indicates that the coating of TiO₂ is predominantly amorphous at low temperature, but small peaks were observed at 2 θ = 25°, 37°. These are associated with diffraction peaks corresponding to anatase crystallites. Figure 3c and Figure 3d show XRD patterns of sol-gel derived TiO₂ powders calcinated at 500 °C and 800 °C, respectively. TiO₂ powder calcinated at 500 °C in the spectrum of TiO₂ can be easily identified as the crystal of anatase form, whereas at 800 °C can be easily taken as the crystal of rutile form.

Figure 3: XRD patterns of samples: (a) pure PAN fibers, (b) TiO₂-covered fibers, (c) sol-gel-derived TiO₂ powder at 500 °C (d) sol-gel-derived TiO₂ powder at 700 °C.

4.2. FTIR spectroscopy analysis

In Figure 4, the IR spectra of the polyacrylonitrile fibers before and after TiO_2 grafting are compared (curves a and b). It is apparent that peaks of the PAN fiber (Figure 4a) can be assigned as follows: 3630 cm^{-1} ($\gamma\text{ OH}$), 2941 and 2870 cm^{-1} ($\gamma\text{ C-H}$ asymmetric and symmetric in CH , CH_2 , and CH_3 groups), 2244 cm^{-1} ($\gamma\text{ C}\equiv\text{N}$), 1741 cm^{-1} ($\gamma\text{ C=O}$), 1455 cm^{-1} ($\delta\text{ CH}_3$ and $\delta_s\text{ CH}_3$), 1374 cm^{-1} ($\delta\text{ CH}_3$ symmetric in CCH_3), 1240 cm^{-1} ($\gamma\text{ C-N}$), 1070 cm^{-1} ($\delta\text{ C-N}$), and 535 cm^{-1} ($\delta\tau\text{ C=O}$), where γ represents a stretching vibration, δ a bending vibration, δ_s a scissor vibration, and δ_τ a twisting vibration [42].

The spectrum of the fibers after grafting (Figure 4b), is substantially unaltered. This means that due to the low external surface area of the supporting fibers, the IR spectroscopy is not informative on the grafting mechanism at all. It is quite remarkable that IR spectrum of the treated sample is totally dominated by the spectrum of the fiber, the contribution of the TiO_2 phase (which should appear at $\gamma < 700\text{ cm}^{-1}$) is also negligible.

Figure 4: FTIR spectra of: (a) pure PAN fibers, (b) TiO_2 -covered fibres

3.4. Thermal analysis

Stabilization of PAN is commonly performed in air between 200 and 300°C . During this process, PAN undergoes a number of physical and chemical changes due to a variety of exothermic chemical reactions, including cyclization, dehydrogenation, oxidation, cross linking and fragmentation. Among them, the cyclization reactions which convert PAN into an infusible stable ladder polymer are of most importance. The cyclization reactions seem not to depend on atmosphere, because they can proceed in either an oxidizing atmosphere or an inert atmosphere. However, as is known that oxygen is necessary for the stabilization of PAN precursor, in order to get high performance carbon fibers, the PAN precursor fibers must be stabilized in an oxidizing atmosphere which is typically air [4]. A greater stability will be obtained when PAN is stabilized in air. This is mainly contributed to the reactions with oxygen. These reactions, mainly including dehydrogenation and oxygen uptake reactions are seriously influenced by the diffusion of oxygen.

3.4.1. Differential scanning calorimetry (DSC) analyses

Figure 5 shows the DSC curves of PAN and PAN/ TiO_2 heated at $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere. PAN exhibits a sharp single exothermic peak initiated at about 235°C and centered at 335°C , as well as PAN/ TiO_2 shows a exothermic peak initiated at about 235°C , and centered at 341°C . The initiation temperature (T_i), finish temperature (T_f), maximum exothermic temperature (T_m), and evolved heat (ΔH) are shown in Table 1. It is known that the cyclization reactions in the PAN follow a free radical mechanism and only can be initiated at a higher temperature. Thus, the single exothermic peak found would be attributed to the overlapping of the free radical cyclization reactions and other exothermic reactions at the higher temperature [43].

Table 1: DSC data for PAN and PAN- TiO_2

Sample	T_i ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH (J.g $^{-1}$)
PAN	235	360	335	391.33
PAN/ TiO_2	235	365	341	366.65

Figure 5: DSC curve of : (A) PAN and (B) PAN- TiO_2

The evolution of a large amount of heat in this case has been attributed to the cyclization of nitrile groups and depends upon nature of the polymer as well as the experimental conditions. Cyclization is highly exothermic process and for pure PAN fibers, is occurred at high temperatures in a narrow range. It has a very high energy release rate, but it is reduced slightly when PAN/ TiO_2 composite are employed. The process of stabilization is achieved by formation of a ladder polymer through nitrile polymerization [1,43].

3.4.2. Thermogravimetric analysis (TGA)

The TGA analysis of the polyacrylonitrile fibre carried out under an air atmosphere and N_2 at a heating rate of $10^\circ\text{C}/\text{min}$. The TGA analysis of the polyacrylonitrile fiber in air atmosphere (Figure 6 and Figure 7) can be roughly divided into three steps according to the extent of weight loss [43-45]. The first step is up to about 250°C , where weight loss is very small. In combination with the DSC results, it is inferred that there is only cyclization occurring in this step, since this reaction theoretically does not cause any weight loss [46]. The second step is up to about 300°C . During this step, the rate of weight loss becomes quite rapid, which is mainly due to the dehydrogenation. It is apparent that the weight loss of PAN/ TiO_2 is larger than that of PAN. It implies that TiO_2 has promoted the dehydrogenation to some extent. In the last step, the rate of weight loss is quite steady; but contrarily the weight loss of PAN becomes larger than that of PAN/ TiO_2 . In this step, on the one hand fragmentation of polymer chains occurs producing volatile particles leading to weight loss.

After combustion of all organic part, the residual amount ($\sim 27\%$ by weight) corresponds to TiO_2 . From this result, it is evident that the TGA technique in air allows to directly evaluating the amount of TiO_2 covering the PAN fibers, as obtained by the synthesis procedure described before.

Figure 6: TGA and DTGA curves of the pure PAN fiber.

Figure 8: TGA and DTGA curves of the pure PAN fiber in N_2 .

Figure 7: TGA and DTGA curves of the TiO_2 -coated fibres in air. The residual weight of the sample, recorded at 800 °C, is related to the TiO_2 content, after that the PAN fiber burning has taken place.

Figure 9: TGA and DTGA curves of the TiO_2 -coated fibres in N_2 .

The TGA analysis of the PAN fiber and TiO_2 -coated fiber in N_2 atmosphere is shown in Figure 8 and Figure 9. The TGA analysis of the TiO_2 -coated fiber shows four decomposition steps [47]. The first appears clearly from TG analysis, and is located between 60-250 °C with mass change of 15% that nearly correspond to the water of hydrous TiO_2 . The second step appears between 250-290 °C with a sudden and intense liberation of heat, corresponding to a mass change of 40%. This exothermic peak is characteristic to the oligomerization of nitrile groups of PAN. The third exothermic peak is located between 290 and 450 °C with mass change of 68%, it may be due to the partial evaporation of NH_3 and HCN. Finally, the fourth exothermic peak located between 450 and 750 °C, corresponding to mass change of 78% may be due to complete evaporation of polymer chain fragments.

The total weight loss for PAN in air up to 800 °C was 95%, in nitrogen only 56%. This big difference is explained by cyclization and carbonization processes which lead to the formation of carbon fibers [44].

3.5. Photocatalytic self-cleaning study

The photoactivity of the titanium dioxide coated PAN fibers has been investigated by exposing the samples containing adsorbed Eosin Y to UV-Vis light. The UV-Vis reflectance spectra obtained on the dried samples before (spectrum a) and after illumination (spectrum b-f) are reported in Figure 10. From Figure 10a, it can be observed that the absorption bands in the 400-600 nm intervals due to adsorption of Eosin Y, change rapidly, because supported TiO_2 promotes the catalytic photodegradation (spectrum b-f). This is not unexpected since the photocatalytic activity of TiO_2 is well known [48, 49]. The disappearance rate of the band due to Eosin Y adsorbed on the TiO_2 -covered fibers is much higher than that observed in case of untreated fibers (Figure 11). Of course the photodegradation effect is lower than that observed on P25 (Figure 12), which is the best TiO_2 catalyst. However, the photocatalytic activity of titania is dependent on both particle size and degree of crystallization [50].

Figure 10: UV-vis reflectance spectra changes of Eosin Y on TiO_2 -coated fibres at room temperature, under UV-Vis light irradiation: no exposure (curve a), irradiation for 2 h (curve b), 4 h (curve c), 6 h (curve d), and 8 h (curve e).

Figure 11: UV-Vis reflectance spectra changes of Eosin Y on pure polyacrylonitrile fibres at room temperature, under UV-Vis light irradiation: no exposure (curve a), irradiation for 2 h (curve b), 4 h (curve c), 6 h (curve d), and 8 h (curve e).

Figure 12: Time dependence of the surface concentration of adsorbed Eosin Y upon light exposure. (A) untreated fibres, (B) Photocatalytic activity of TiO_2 -coated fibres, and (C) P25.

To test the durability of photocatalytic activity of the TiO_2 -coated fibres, the photodegradation process was repeated for three more cycles on the same

sample. Figure 13 shows the photocatalytic efficiency of the TiO_2 -modified fiber for the photodegradation of EY, which is unchanged relatively upon repeating cycles. These results suggest that TiO_2 losses from the fibers surface for each impregnation of stain (EY) is ignorable and TiO_2 particles were adhered compactly to the fibers.

Figure 13: Photocatalytic efficiency of TiO_2 -modified PAN fibers upon repeated EY adsorption-illumination cycles.

From all these data, it is evident that supported TiO_2 particles promote the photodegradation process and the high surface area associated with the small particle size ensures a favorable condition for a relatively fast degradation and performance of self cleaning.

4. CONCLUSION

Anatase nanocrystals were successfully synthesized and deposited on polyacrylonitrile fibres with significant photocatalytic self-cleaning activity using the sol-gel process. The TiO_2 nanoparticles, have been found to form a homogeneous thin film on the fiber surface, which shows efficient photocatalytic properties when exposed to UV-Vis light. Self-cleaning properties were monitored by diffuse reflectance spectroscopy. The TiO_2 -covered polyacrylonitrile fibres show high photocatalytic efficiency in decomposing the pre-adsorbed Eosin Y under UV-Vis light. TiO_2 -covered fibers promote the photodegradation process and the high surface area associated with the small particle size ensures a favorable condition for a relatively fast degradation. The TGA curve of PAN/ TiO_2 showed a slight increase of weight loss in the second step and a significant decrease of weight loss in the third step. It implied that the dehydrogenation and oxygen uptake reactions would be promoted by the TiO_2 to some extent. Cyclization is highly exothermic process and for pure PAN fibers, is occurred at high temperatures in a narrow range. It has a very high energy release rate, but it is reduced slightly when PAN/ TiO_2 composite are employed.

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