RESEARCH PAPER

Photocatalytic Removal of NOx Gas from Air by TiO_2/Polymer Composite Nanofibers

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ABSTRACT

Nitrogen oxides (NOx) released in atmosphere by fuels combustion lead to photochemical smog and acidic rains and have negative effects on human`s nervous system. In this research, nanocomposite membranes of poly vinylidene fluoride (PVDF)/poly dimethylsiloxane (PDMS), and titanium dioxide nanoparticles (TiO_2) with different weight percentages of TiO_2 (0.5 and 1) were prepared for adsorption of NOx using electrospinning. To investigate the properties of prepared fibers, scanning electron microscopy (SEM) and attenuated total reflectance spectroscopy (ATR) were used. The fibers morphology and particles distribution in polymer were determined by SEM pictures. The composite fibers with 0.5 wt% TiO_2 removed 50% nitrogen oxides, and fibers with 1 wt% TiO_2 removed 100% of nitrogen oxides. Generally, titanium dioxide nanoparticles on surface of fibers in presence of water vapor under ultraviolet irradiation caused to remove toxic NOx gas by photocatalysis process. The ATR spectrum of fibers confirmed NOx adsorption by composite nanofibers. TiO_2/polymer composite membrane showed the promising potential for application as a filter to remove nitrogen oxides from air.

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INTRODUCTION

Nowadays, regarding to industrialization of societies and increasing consumption of fossil fuels, contaminants and harmful gasses have increased in air of metropolises and cities. These contaminants cause global warming, ozone layer perforation, threating human health, etc. Excessive inhalation (aspiration) of these gases can cause respiratory disease and even early death [1]. These problems duplicated in industrial cities. The scientists have looked for new ways to remove these pollutants.

Formerly, common methods such as adsorption and reduction of NOx by aminated solvents in the presence of catalyst or adsorption were used to remove NOx. These methods, however, are high cost and time consuming, so, scientists have proposed alternative methods which are cost effective, fast and more efficient. In recent years, removal of contaminants and toxic gaseous nanocomposites has attracted a lot of interest as these materials are cost effective, adaptable and ecofriendly [2].

The direct and indirect effects of nanotechnology on air purification and decrease of pollutants are considerable from different aspects.

Nanotechnology offers facilities to produce novel materials, instruments and systems by

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taking control the atomic and molecular level and utilization of apparent properties which are revealed at this level. Synthesis of nanobiomaterials, nanotubes, nanocomposites, nanofilters and nanoparticles are some examples of nanotechnology employed to solve the environmental issues and prevent air pollutions. There are different cases of nanostructure applications to protect environment; for example, nanofilters for industrial waste water treatment, nanopowders for purification of exhaust pollutants from automobiles and factories, and nanotubes for saving H_2 as clean fuel. The extensive use of nanocomposites, nanocrystals, and nanosensors can reduce the consumption of 1.5 billion liters of gasoline per year for vehicles, and decrease CO_2 emission to atmosphere by more than 5 million kilogram per year [3].

The concentration of nitrogen oxides, NOx, is measured because of the negative effect of NOx on human health and their contribution in smog and acid rains [4]. In accordance with medical research, nitrogen oxides affect human nervous system and its concentration in blood plasma is measurable. Nowadays, NO (nitrogen monoxide) and NO_2 (nitrogen dioxide) are emitted to atmosphere by combustion of fossil fuels in internal combustion motors [5]. One of the efficient methods to remove NOx gas is photocatalytic process of semiconductors. For the first time, Fujishima and Honda discovered this process in 1972, after which many researchers dedicated their investigations to explore the mechanism of photocatalytic performance of TiO_2 and other semiconductors[6-8]. Basically, the mechanism of the photocatlytic process is explained by the ability of semiconductor material to form an electron- hole pair under light irradiation, then free radicals are produced which result in secondary reactions [9]. The reaction of free radicals with pollutants in gas or liquid phase degrades them by oxidation or reduction processes [10]. The required energy to produce electron-hole pair depends on the band gap of semiconductor. The required energy to make electron/hole pair in TiO_2 with 3.2 eV band gap is provided by ultra violet radiation [11]. Different strategies are used to improve photocatalytic efficiency, such as synthesizing narrow band gap photocatalysts, decreasing electron/hole recombination, and enhancing adsorption ability of photocatalysts. TiO_2-saponite nanocomposite was synthesized by solvothermal reaction, and its photocatalytic activity in decomposing NOx gas was investigated. The good NOx removal performance of TiO_2-saponite could be related to proper dispersion of titania on saponite surface [12]. Activated carbon fibers are effective for removing NOx in the presence of NH_3. They have high surface area and uniform distribution of pores [13]. Carolina et al. (2014) prepared activated viscous fibers (AVF) to remove NO and SO_2 [14]. The AVF showed a satisfactory performance in the removal of contaminants and good compatibility with other synthetic fibers. Lin and his coworker prepared nanofibers by electrospinning and adsorbed CO_2 gas. The obtained fibers in this research showed the hydrophobic properties. The water contact angle of these fibers was about 140° that reached 150° after modification by AFS. These fibers adsorbed CO_2 for 4 days and were reusable [15]. Todorova et al. synthesized TiO_2/graphene nanocomposite photocatalyst via solvothermal process. Reduced graphene oxide and surfactant-stabilized graphene were used for preparation of two types of composite and their photocatalytic activity in NOx oxidation, and light irradiation were investigated. TiO_2 with reduced graphene oxide removed NOx completely. It could be attributed to separation of electron- hole through interfacial charge transfer [16]. Iron containing catalysts have found applications in effective removal of air pollutants due to their low toxicity and high natural abundance. Carbon quantum dots (CQDs) modified FeOOH nanocomposites showed enhanced NO removal and decreased toxic intermediate generation, due to their effective charge separation in composite [17]. The presence of Pd atoms on surface of TiO_2 particles enhances its solar photocatalytic NOx removal. NO removal efficiency linearly increases with the mass fraction of isolated Pd atoms on the surface of TiO_2 particles. This improved performance is related to the high resistance of Pd sites to nitrate poisoning [18]. The combination of TiO_2 and urea on the activated carbon fibers removes atmospheric NO to harmless N_2 [19].

In this project, poly vinylidene fluoride and poly dimethyl siloxane with TiO_2 nanoparticles are used to synthesize polymeric nanocomposites for adsorption pollutants. The main goal of this research is removal of dangerous and toxic NOx by spun fibers. The fibers are prepared with electrospinning. To our knowledge, this is the first time that these fibers are studied for NOx degradation.

EXPERIMENTS

Materials and Instruments

Poly vinylidene fluoride (PVDF) and poly dimethylsiloxane (PDMS) were bought from Kynar and Dow Corning, respectively. Dimethylformamide (DMF) was obtained from Merck. All reagents were used without any purification. Titania nanoparticles with average dimeter of 20 nm were purchased from Pishgaman. Scanning electron microscope (SEM) model EM3200 and Fourier transform infrared spectrometer (FTIR) model Jasco 6300 were used to characterize the composite nanofibers. The lx testo350 equipment was used to determine NOx concentration in air.

Producing the nanofibers was done by electrospinning machine in nanotechnology and advanced materials institute (NAMI). This machine was equipped with power supply, syringe and collector. Fig. 1 shows the electrospinning machine.

Preparation of TiO_2 / polymer composite

PVDF and PDMS were mixed together in 3:2 weight portions. Then, DMF as a solvent was added to polymeric mixture and stirred till homogeneous solution was obtained. 0.5 wt% and 1 wt% TiO_2/ polymer composites were prepared with addition of 0.5 w/w% and 1w/w% of TiO_2 nanoparticles to homogenous polymeric solutions, respectively, and stirred for 18 hours on magnetic stirrer.

Spinning fibers from TiO_2 / polymer composite

The composite mixture was delivered at a constant flow rate (1mL/h) to syringe pump. The distance between collector and nozzle was determined at 20 cm. Upon applying a high voltage (200 kV), a fluid jet was ejected from the syringe. Solvent was evaporated as the jet accelerated toward fixed collector. Charged composite fiber was deposited on collector in the form of non-woven fibers. The fibers of 0.5 wt% and 1 wt% TiO_2/ polymer composites and polymer without TiO_2 were collected separately for 30 min.

Characterization

To investigate the morphology, quality and diameter of fibers and porosity of felt, the scanning electron microscopy (SEM) analysis was used. To investigate the functional groups on surface of nanofibers before and after of NOx removal test, attenuated total reflectance spectroscopy (ATR) was used.

NOx Removal Test

To evaluate capability of composite nanofibers to removal of NOx from air, the collected spun fibers during 30 min on Al foil was kept on closed container under N_2 atmosphere. Regarding To lx testo350 instruction for use, a device was made by the researchers. Fig. 2 shows this device. This device is a glass made cube with two aligned circle vents. A vent with 12 cm diameter is equipped with a ventilator. The vent with 6 cm diameter is used to stabilize membrane.

To investigate NOx removal by membrane, one of the most polluted and crowded region of Isfahan city from the point of Isfahan Department of environment was chosen as a test location. All of NOx removal tests were done at 1 pm and in sunny days. The NOx concentration in air was measured at first. Then, the fresh membrane was stabilized

Fig. 1. The electrospinning machine in nanotechnology and advanced materials institute.

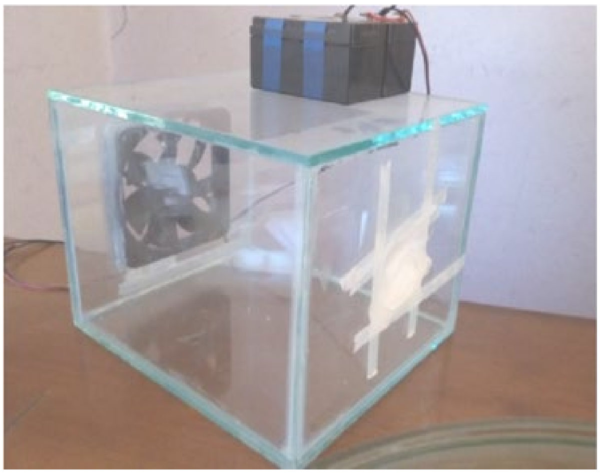

Fig. 2. The device fabricated for stabilization of membrane and NOx removal test.

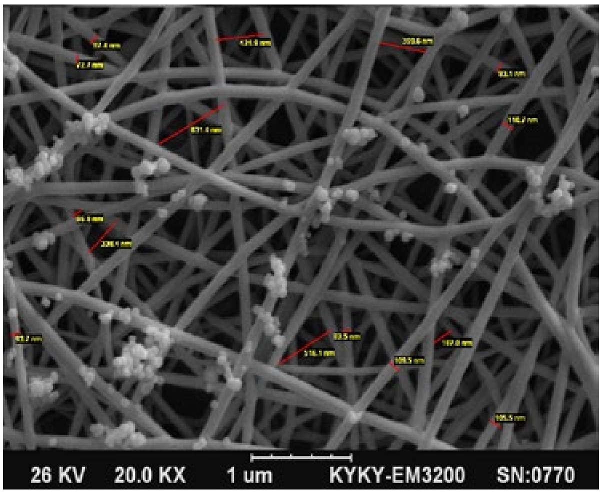

Fig. 3. SEM image of electrospun fibers from 0.5 wt% TiO_2-containing composite.

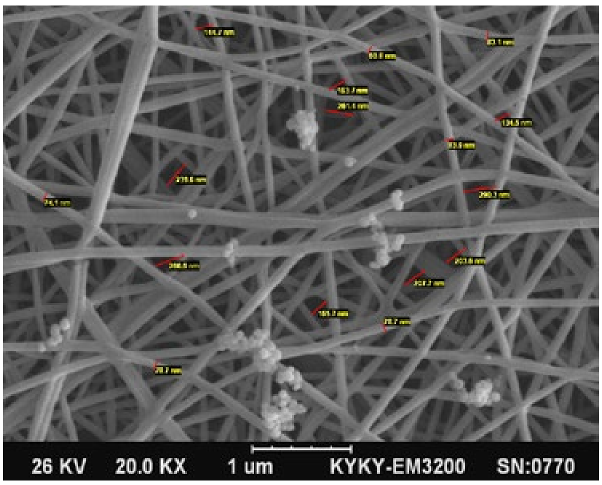

Fig. 4 SEM image of electrospun fibers from 1 wt% TiO_2-containing composite.

Table 1.The Results of NOx removal test by spun fibers membrane from TiO_2/polymer composites.

Name of membrane	Nox degradation percent
0.5 wt% TiO_2/ polymer	50%
1 wt% TiO_2/ polymer	100%

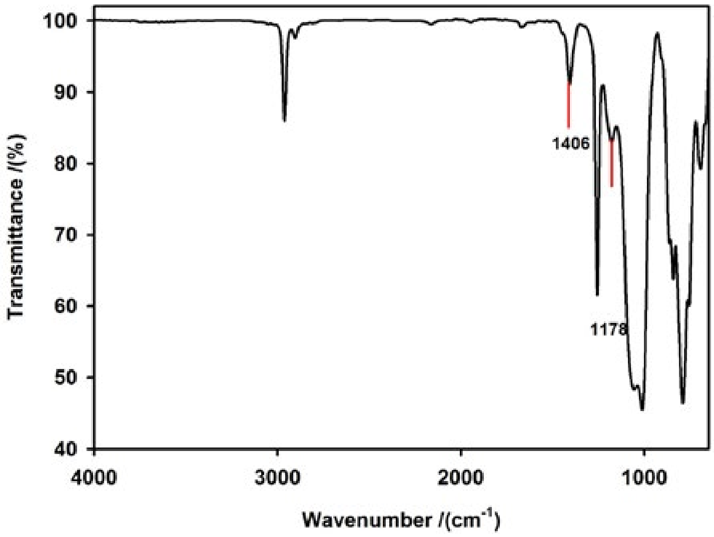

Fig. 5. ATR spectrum of electrospun fibers from 0.5 wt% TiO_2-containing composite before NOx removal test.

in its place, and then, NOx concentration in air passed through membrane was measured again. The membrane efficiency in NO_X removal was calculated from Equation 1,

$$R\% = \frac{C_i - C_s}{C_i} \times 100 \quad (1)$$

where C_i is the initial concentration of NOx (NOx concentration in air stream) and C_s is the secondary concentration of NOx (NOx concentration in air stream passed through membrane) and is membrane efficiency in NOx removal or NOx degradation percent.

RESULTS AND DISCUSSION

Figs. 3 and 4 show scaninig electron microscope pictures of 0.5 wt% and 1wt% TiO_2 containing composite, respectively. Regarding to SEM picture, the fiber diameter of 0.5 wt% composite was between 72.7-109.5 nm, and the made membrane from spun fibers had porous texture (Fig. 3). The diameter of fibers spining from 1wt% TiO_2-containing composite was obtained between 60.8- 83.9 (Fig. 4). SEM pictures show that nanoparticles are on the surface of fibers which provide good substrate to photodegradade of NOx. furthurmore sem images reval that the fibers have uniform diameter. The porous texture of membrane makes possible air passingthrough the membrane. The results of NOx removal test are summarized in Table 1.

It seems that during NOx removal by TiO_2 nanoparticles under sun light irradiation, valance band electrons are excited and transfered to conduct band. Due to this energy transition , a hole is created in valance band and an electron remains in conduct band. The hole in reaction with water vapor produces hydroxyl radicals. Hydroxyl radicals react with NOx and acid nitric is obtained as represent in Equations 2-5.

$$TiO_2 + hv \rightarrow e^- + h^+ \quad (2)$$

$$e^- + O_2 \rightarrow O_2^- \quad (3)$$

$$h^+ + H_2O \rightarrow OH^* + H^+ \quad (4)$$

$$NO_x + 3OH^* \rightarrow NO_3^- + H^+ \ (HNO_3) \quad (5)$$

The increase in the amount of TiO_2 nanoparticles in composite leads to a better NOx removal because of providing more action sites to adsorb NOx from air and secondary reactions.

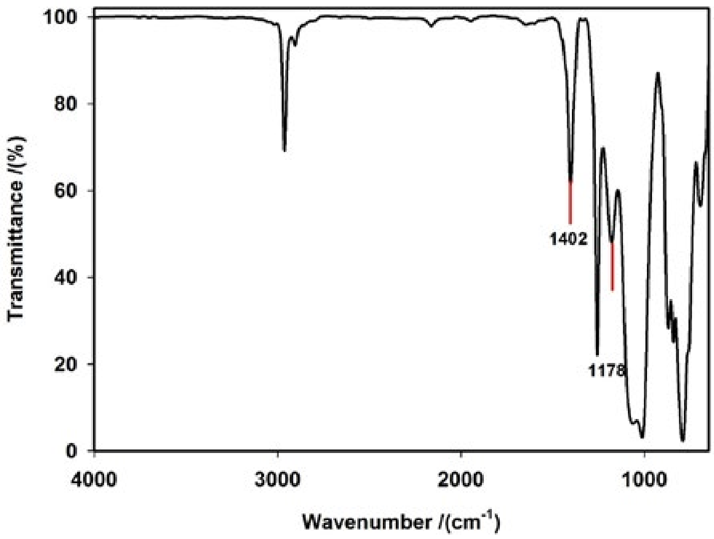

Fig. 6. ATR spectrum of electrospun fibers from 0.5wt% TiO_2-containing composite after NOx removal test.

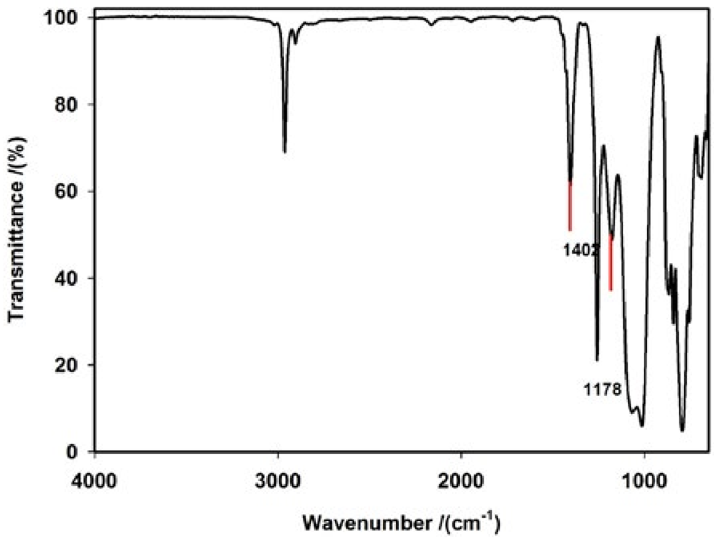

Fig. 7. ATR spectrum of electrospun fibers from 1wt% TiO_2-containing composite after NOx removal test.

To investigate and confirm NOx adsorption by spun fibers, the ATR spectrums of composite before NOx removal (Fig. 5) and after NOx removal (Figs. 6 and 7) were prepared. The peaks at 1402 cm^{-1}, 1177 cm^{-1} and 1178 cm^{-1} in Figs. 5, 6 and 7 are attributed to O−N and H−N, supporting HNO_3 formation and NOx removal by photo induced reactions[16].

CONCLUSION

We have synthesized the effective membrane to remove NOx gas from air spun fibers. The porous texture of membrane and presence of TiO_2 nanoparticles on surface of fibers coopreate for succesful removal of NOx. This research shows the potential application of TiO_2/ polymer composite membrane as a filter to purify NOx-polluted air.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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