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A facile method to prepare polyvinylidene fluoride composite nanofibers with high photocatalytic activity via nanolayer coextrusion

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ABSTRACT

The agglomeration of powder photocatalysts for water remediation can reduce the catalytic efficiency, and the difficulty to be recycled will cause the secondary pollution. A facile method suitable for volume production of polyvinylidene fluoride (PVDF)-based nanofibers as well as mat with high photocatalytic activity is proposed via nanolayer coextrusion, which is a new top-down method. Hydrophilic TiO_2 and acidified multi-walled carbon nanotubes (MWCNTs) are used for the preparation of highly active PVDF photocatalysts. The preparation process is eco-friendly, and no organic solvents are used. The morphology and structure of PVDF/(TiO_2/MWCNTs) composite nanofibers are investigated on scanning electron microscope and transmission electron microscope. X-ray diffraction patterns confirm that TiO_2 is still anatase on nanofiber surface after melting processing. PVDF/(TiO_2/MWCNTs) composite nanofibers exhibit high photocatalytic efficiency for the degradation of methylene blue in water. In photoluminescence and ultraviolet spectra, the red shift phenomenon of the absorption peak of the nanofibers is observed. It is found that MWCNTs can improve the photocatalytic efficiency of TiO_2 in PVDF composite nanofibers, in which MWCNTs can be aligned along the naofibers and play a role as the bridge among TiO_2 particles and enhance the transfer of electrons. This facile and high efficient method can be widely used for the volume production of various kinds of similar functional nanofibers in the future.

1. Introduction

Since the discovery of photocatalytic activity, titanium dioxide (TiO_2) has been regarded as one of the most promising catalysts, sensors, and high performance photovoltaics, which has received enormous scientific interest [1–4]. Particularly, TiO_2 photocatalysts for the water remediation have been concerned, in which a large amount of photocatalysts are required [5–8]. However, for TiO_2 photocatalysts, the fundamental problems in practical application include the ineffective utilization of natural visible light and the fast electron-hole recombination rate. In addition, > 90% of the photogenerated electrons will recombine with photogenerated holes promptly after photoexcitation in bulk TiO_2 crystal [9,10]. One of the approaches is to modify TiO_2 with photosensitive semiconducting materials either available in natural visible light or slow down the electron-hole recombination [11]. Carbon nanotubes (CNTs) is one of these promising materials with the benefit of high aspect ratio, large surface area, chemical stability, faster electron transfer rate, and the synergic effects with TiO_2 [12–15]. Di et al. [6] synthesized TiO_2/CNTs composite photocatalysts with a tree shape by a one-step solvothermal method. The composites have high light-harvesting efficiency and low electron-hole recombination rate. TiO_2 anchored CNTs by employing sol-gel process was also reported [3,16,17]. This special structure guarantees a sufficiently rapid transport of electrons. Gui et al. [18] prepared TiO_2/MWCNTs core-shell nanocomposites from an efficient coating approach, and the nanocomposite can be excited by visible light. Wang et al. [19] synthesized 3D mesoporous TiO_2/CNTs nanocomposite by using a facile polyethylene oxide (PEO)-aided self-assembled process. The nanocomposite retained high electronic conductivity of CNTs. Yao et al. [13] prepared TiO_2/CNTs composite by a simple evaporation and drying process, and water was used as dispersion medium. The TiO_2/CNTs arrangement can stabilize charge separation and reduce charge recombination.

Nevertheless, whether pure TiO_2 or TiO_2/CNTs composites are used in practical application, the powder catalysts are easy to agglomerate and difficult to be recycled. The agglomeration of photocatalysts can reduce the catalytic efficiency [20,21], and the recycling problem will cause secondary pollution [22]. In order to solve the problems of TiO_2 recovery and agglomeration, TiO_2 is typically prepared into fibers and the electrospinning technology is the most widely used [23–26]. However, the efficiency to prepare electrospinning fibers is relative lower, and it is difficult for volume production [27]. Most of the cases

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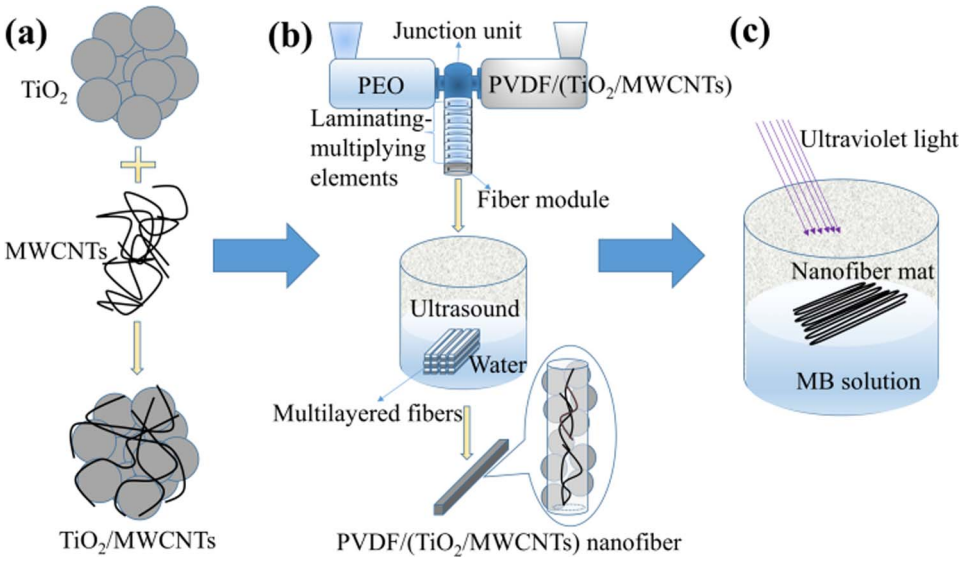

Fig. 1. The processing method with high efficiency for photocatalytic PVDF/TiO_2 or PVDF/(TiO_2/MWCNTs) nanofibers, (a) TiO_2/MWCNTs composites, (b) nanolayer coextrusion, and (c) photocatalytic degradation of MB solution under UV light.

need a large amount of organic solvents, which may pollute the environment [28]. In addition, most of electrospinning TiO_2–based fibers need a post-processing, such as calcinations [29–32]. This will increase the difficulty and cost of preparation.

The multilayer coextrusion is a low-cost method in a continuous melt process to fabricate large-area polymeric microlayer films. Two or three polymers can be combined into a continuous alternating layered structure by the microlayer or nanolayer coextrusion. Due to hundreds or thousands of layers in a film, the thickness of the individual layer can be adjusted from microscale to nanoscale [33,34]. When the individual layer thickness was micron-sized or nanometer-sized, the multilayered film can be called microlayer or nanolayer, respectively. The nanolayered structure can be further cut vertically into nanosized fibers via a specially-designed exit cutting die. A post-processing orientation procedure can help further decrease the cross-sectional dimension of the fibers. This preparation process is high efficient, eco-friendly, and no organic solvents are used [35–38]. Particularly, MWCNTs can be aligned well in the confined nanospace of polymer melts via the nanolayer coextrusion [39]. Due to the good mechanical and membrane-forming properties, as well as high chemical stability [40–42], polyvinylidene fluoride (PVDF) has been used as the matrix for various kinds of optical stable materials. In the present study, the nanolayer coextrusion is used to prepare PVDF/(TiO_2/MWCNTs) composite nanofibers. The nanofibers as well as nanofiber mats are expected to have better photocatalytic effects than pure TiO_2. In addition, the problems of TiO_2 recovery and agglomeration can be well resolved.

2. Experimental

2.1. Materials

PVDF (DS 206, melt index (MI) = 8.5 g 10 min^{-1}, 210 °C, 2.16 kg) was purchased from Shandong Huaxiashenzhou New Material Co.. PEO (PEO-1, MI = 7.8 g·10 min^{-1}, 210 °C, 2.16 kg) was purchased from Sumitomo Seika Trading (Shanghai) Co.. H_2SO_4 (98%) and HNO_3 (65%) were purchased from Sigma Aldrich Co.. TiO_2 (> 99.8%, anatase powder, hydrophilic, diameter 100 nm) was purchased from Greagent Co.. MWCNTs (TNIM1, > 95%, outer diameter 15–20 nm) was obtained from Chengdu Organic Chem. Co.. Methylene blue (MB) ($C_{16}H_{18}ClN_2S·3H_2O$, > 99.7%) was purchased from Aladdin Chem. Co.

2.2. Preparation of TiO_2/MWCNTs composites

TiO_2/MWCNTs composites were prepared by a simple evaporation and drying process similar to the method in Ref. [13]. TiO_2 and MWCNTs were dried separately in a vacuum oven at 70 °C for 24 h before accurately weighed. Firstly, MWCNTs were treated in an ultrasonic system (60 °C, 3 h) with mixed acid (HNO_3:H_2SO_4 = 1:3, v/v) to acidize MWCNTs, which were functionalized with −COOH and −OH [43]. Then, 1 g MWCNTs were dispersed in deionized water in a 1 L beaker and sonicated for 30 min. 20 g TiO_2 powders (TiO_2:MWCNTs = 20:1, w/w) were added to the suspension while stirring [12]. After additional sonication for 30 min, the mixed suspension was heated to 80 °C in an open flask with stirring to accelerate the evaporation of water. After the water evaporated, the product was dried in a vacuum oven at 100 °C for 24 h.

2.3. Preparation of PVDF/TiO_2 and PVDF/(TiO_2/MWCNTs) nanofibers via nanolayer coextrusion

Prior to processing, PVDF, PEO, TiO_2, and TiO_2/MWCNTs were dried separately in a vacuum oven at 50 °C for 24 h. First of all, TiO_2 or TiO_2/MWCNTs powders were blended with PVDF in HAAKE mixer (HAAKE Rheocord 9000) with rotational speed of 60 rpm at 210 °C for 15 min to produce PVDF/TiO_2 or PVDF/(TiO_2/MWCNTs) (10, 20, 30, and 40 wt%) composites. After this, the composites were separately smashed into pellets through a shredding machine. PEO powders and PVDF/TiO_2 (or PVDF/(TiO_2/MWCNTs)) pellets were fed into two different single-screw extruders respectively, with an average processing temperature of 210 °C, and coextruded through a series of multiplier elements similar to those of microlayer extrusion [34]. PEO was used as isolation layers between PVDF/TiO_2 (or PVDF/(TiO_2/MWCNTs)) layers. After the formation of the nanolayered structure, PEO/PVDF/TiO_2 or PEO/PVDF/(TiO_2/MWCNTs) multilayered nanofibers were produced via a cutting die for the fibers, and then ultrasonically processed in deionized water at room temperature for 3 h to dissolve PEO isolation layers, as shown in Fig. 1. Then, PVDF/TiO_2 and PVDF/(TiO_2/MWCNTs) nanofibers were dried in a vacuum oven at 70 °C for 24 h. Finally, the nanofibers were pressed (10 MPa, room temperature) into mats (thickness = 0.1 mm) by a press machine before photocatalytic tests, and the area of the mat depends on the titanium dioxide content.

2.4. Characterization

Ultrasonic cleaning machine (KM-410C) (frequency: 40 KHz; ultrasonic power: 200 W; liquid volume: 10 L) was used to dissolve PEO in deionized water at room temperature. In order to ensure dissolution efficiency and temperature stability, the deionized water was replaced

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