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A novel and highly photocatalytic “TiO_2wallpaper” made of electrospun TiO_2/bioglass hybrid nanofiber

He Lian, Zhaoxu Meng*

Department of Biomedical Engineering, Faculty of Medical Instrumentation, Shenyang Pharmaceutical University, No. 103, Wenhua Road, Shenyang 110016, China

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ABSTRACT

Over the past years, the high catalytic property of electrospun nanofibers attracted more attention in the field of catalysis. Titanium dioxide (TiO_2) electrospun nanofibers and their modifications have become the focus of the photocatalysis research owing to their high surface to volume ratio, high porosity and non-toxicity. So far, however, it has not been applied in the photocatalytic devices because the bad self-supporting is still the main drawback to prevent their practical application. Here, a novel three-dimensional porous membrane of hybrid TiO_2/bioglass, which could be adhered on different carriers as “wallpaper” only by a short time of heating, has been fabricated in this work. Though microfluidic electrospinning, the hybrid nanofibrous membrane could be divided into three thin layers according to the components of the fiber. The top layer of the hybrid nanofibrous membrane, containing 90% TiO_2 in the fiber, would maintain three-dimensional interconnected porous structure with the increasing of its thickness, revealing highly photocatalytic activity. In addition, the bottom bioglass ($70SiO_2{\cdot}25CaO{\cdot}5P_2O_5$) nanofibrous layer of the hybrid TiO_2/bioglass membrane made the membrane adhere on different carriers firmly through heating within 5 s. The hybrid membrane exhibited higher photocatalytic efficiency than the thin film of TiO_2, which would be expected to be used in the preparation of photocatalytic devices.

1. Introduction

Due to the increasing demand for environmental protection, photocatalysis has become a focus of interest because it is a safe and green method for pollution treatment. The commonly used semiconductor photocatalyst titanium dioxide (TiO_2) can degrade a large range of pollutants into carbon dioxide and water under UV light irradiation. Moreover, TiO_2-based photocatalysis presents many advantages such as low energy consumption and simple manipulation. Although TiO_2 exhibits a catalytic activity, extensive efforts have been shown to improve its photocatalytic efficiency by preparing it as nanoparticles, nanofilms, and nanofibers [1–3]. Indeed, TiO_2 nanoparticles present a high surface to volume ratio, which increases the number of active sites to react with pollutants. However, the use of nanoparticles is limited due to particle agglomeration and difficult subsequent separation. Alternatively, TiO_2 nanofilms, which are prepared by direct coating of the TiO_2 nanoparticles on the surface of the reactor, present low porosity.

In contrast, electrospun TiO_2 nanofibers have a high specific surface to area ratio, thus increasing the number of active sites. For example, Li et al. demonstrated that the photocatalytic efficiency of TiO_2 electrospun fibers was higher than that of commercial P-25 TiO_2 nanoparticles [4]. In addition, a membrane that is composed of TiO_2 nanofibers presents a high porosity and many interconnected pores, which further increase the surface area able to react with more pollutants. However, TiO_2 electrospun membranes are rarely used in photocatalysis devices, since TiO_2 nanofibrous membranes are easily breakable when submitted to external stress because of the brittle TiO_2 nanofibers [5]. The flexibility of TiO_2 nanofibers could be increased by doping elements into TiO_2 nanofibers or blending other type of nanofibers with TiO_2 but only to a certain extent [6,7]. Moreover, it was difficult to combine the TiO_2 electrospun nanofiber with other carriers or devices. We have previously reported the use of polydimethylsiloxane (PDMS) glue bonding TiO_2 electrospun fiber and glass; but the glue layer must very thin, or glue would cover the fiber, reducing the photocatalytic efficiency [8].

In this work, we presented a novel strategy to fabricate a three-dimensional membrane composed of multi-layered hybrid electrospun nanofibers with different ratios of TiO_2/bioglass ($70SiO_2{\cdot}25CaO{\cdot}5P_2O_5$). Bioglass as a non-toxic inorganic noncrystalline material only has a softening point, and the viscosity of bioglass can be increased over the softening point, enabling the combination of the membrane with other carriers by simple heating treatment. Since the combination process

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* Corresponding author.
E-mail address: mengzhaoxu2006@163.com (Z. Meng).

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was similar to the behavior of pasting wallpaper, we called the membrane “TiO_2 wallpaper”. In consequence, the “TiO_2 wallpaper” would be strengthened by the carrier and resistant to external shocks, thus avoiding the risk of breakage. In addition, the hydrophilic property of the bioglass would enhance the wettability of the hybrid nanofibers, improving the photocatalytic activity of the “TiO_2 wallpaper”.

2. Experimental

2.1. Materials

Poly(vinyl pyrrolidone) (PVP, 1 300 000 Da), tetraethyl orthosilicate, and triethyl phosphate were purchased from Aladdin Reagent Company (China). TiO_2 nanoparticle (size: 25 nm, anatase) was purchased from Shanghai Macklin Biochemical Co., Ltd. Polydimethylsiloxane (PDMS, Sylgard 184) was provided by the Dow Corning Company (USA). SU-8 photoresist was purchased from MicroChem Corp. (USA). All the other chemicals were of analytical reagent grade.

2.2. Preparation of the TiO_2 precursor

Ethanol and glacial acetic acid were mixed at a volume ratio of 4:1. Then, tetrabutyl titanate was dissolved in the prepared mixture at a volume ratio of 1:5. When the solution was clear, PVP was added into the reactive mixture under stirring at room temperature to obtain a final concentration of 80 μg mL^{-1}.

2.3. Preparation of the bioglass precursor

Tetraethyl orthosilicate, calcium nitrate, and triethyl phosphate at a suitable molar ratio ($70SiO_2{\cdot}25CaO{\cdot}5P_2O_5$) were mixed in ethanol. The catalyst hydrochloric acid (HCl, 1 mol L^{-1}), was added to the mixture at a volume ratio of 1:50. The solution was stirred continuously for 12 h followed by an aging period of 48 h at 40 °C. Prior to electrospinning, the bioglass precursor solution was mixed with PVP/ethanol solution (0.08 g mL^{-1}) at a volume ratio of 1:1.

2.4. Fabrication of the microfluidic electrospinning chip

Firstly, the PDMS substrate presenting microchannels was fabricated by soft lithography. In brief, the glass substrate was treated with a piranha wet etch (H_2SO_4: H_2O_2 $v{:}v = 3{:}1$) followed by a washing with de-ionized water and subsequent dehydration (180 °C, 2 h). In addition, the glass substrate was spun coated by SU-8 photoresist (600 rpm for 30 s then 1000 rpm for 30 s), and submitted to a series of established steps including soft bake, exposure under UV light with a designed mask, post exposure bake, removal, and hard bake. The PDMS substrate was then formed by pouring the prepolymer (10:1) into the SU-8 template and cured at 80 °C for 1 h. Finally, the PDMS substrate was gluing on the glass piece with diluted PDMS (PDMS: methylbenzene $v{:}v = 2{:}3$). In particular, the stainless steel blunt needle was inserted into the microchannel and the gap was sealed with a solution of diluted PDMS. The chip was then dried in vacuum for 4 h followed by a heating step at 80 °C for 1 h.

2.5. Electrospinning

The microfluidic electrospinning system was composed of a microfluidic chip, two separate infusion pumps, and a computer that monitored the feeding rate of the infusion pump. For electrospinning, two plastic syringes loaded with 5 mL of TiO_2 precursor solution (solution 1) and bioglass precursor solution (solution 2) were fastened on the two separate infusion pumps. The stainless-steel blunt needle was connected to the high-voltage supply. Under pre-determined flow rates (top layer: 0.45 mL h^{-1} of solution 1 and 0.05 mL h^{-1} of solution 2; middle layer: 0.25 mL h^{-1} of solution 1 and 0.25 mL h^{-1} of solution 2; bottom layer: 0.5 mL h^{-1} of only solution 2) and the two solutions were homogeneously mixed through the serpentine microchannel. When a voltage of 10 kV was applied, the jet was ejected from the needle and the precursor nanofibers were collected on the target, which was placed 10 cm away from the needle. The precursor nanofibrous membrane dried under vacuum for 24 h at 40 °C followed by a heating step at 500 °C for 2 h to burn all organic compounds contained in the membrane. Finally, the “TiO_2 wallpaper” was removed from the muffle furnace and stored in a dry environment.

2.6. Preparation of the TiO_2 film

TiO_2 nanoparticle was mixed in the TiO_2 precursor colloid at a concentration of 0.01 g mL^{-1}. The mixture was then spun coated onto a glass slide ($10 \times 10\ mm^2$) at a rotation rate of 1000 rpm for 30 s, followed by drying at 80 °C for 1 h. After repeating several times the step, the glass slide was placed into the muffle furnace for calcination (500 °C, 2 h). The furnace was the same one used for the preparation of the TiO_2 nanofibers. Finally, the glass slides with different coating layers were stored in a dry environment.

2.7. Characterization

The morphologies of the hybrid fibers were characterized by scanning electron microscopy (SEM) (FE-SEM Model JSM-7011F, Japan). All the samples were dried under vacuum for 24 h and then coated with a thin layer of gold prior to analysis. The diameters of the resulting fibers were analyzed using the software Image J. The surface roughness of the fiber was also evaluated by Atomic Force Microscopy (AFM, Bruker Multimode 8, Germany). The thickness of the membrane was measured by micrometer. The Brunauer–Emmett–Teller (BET) special surface area was evaluated by Surface Area and Mesopore Analyzer (JW-BK112, China). X-ray diffraction analysis was performed with an X-ray diffractometer (Bruker D8 Advance, Germany) equipped with Cu-Kα source and operating at 40 kV and 100 mA. The diffraction patterns were obtained at a scan rate of 1°/min.

2.8. Photodegradation experiment

The photodegradation system is shown in Fig. S1 (Support information). Prior to the experiment, different thicknesses of the top layer of “TiO_2 wallpaper” were produced by collecting at different times (15, 30, 45, 60 min). In this experiment, 50 mL of methylene blue solution (10 mg L^{-1}) was contained in a reactor equipped with a peristaltic pump that was used for circulating the solution (flow rate: 10 mL min^{-1}). The UV irradiation was provided by a UV-LED (365 nm, 40 mW cm^{-2}). The samples were immerged in the methylene blue solution for 60 min to reach the adsorption-desorption equilibrium. Then, the samples were exposed to UV light for 60 min. At a specific time (15, 30, 45, 60 min), the discoloration of methylene blue solution (1 mL) was analyzed with a UV–visible spectrophotometer (664 nm).

3. Results and discussion

The fabrication procedure of the “TiO_2 wallpaper” is illustrated in Fig. 1. Firstly, the hybrid composite nanofibers, as precursor of the “TiO_2 wallpaper”, were produced by a microfluidic electrospinning system, in which the injected volume of TiO_2 precursor solution and bioglass precursor solution could be adjusted separately [9]. After calcination at 500 °C for 2 h, the precursor nanofibrous membrane was transformed into “TiO_2 wallpaper”. Subsequently, the “TiO_2 wallpaper” was combined to the carrier by heating for several seconds via a cassette flamethrower, allowing the bottom layer of the bioglass nanofibers to melt and adhere on the surface of different carriers such as glass or copper plate (Fig. S2, Support information).