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Effect of oil on the morphology and photocatalysis of emulsion electrospun titanium dioxide nanomaterials

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ABSTRACT

The effect of different oil on morphologies of emulsion electrospun products has been systematically studied. High photocatalytic degradation performed titanium dioxide (TiO_2) nanomaterials with diverse morphologies, including nanoparticles, nanofibers, necklace-like nanofibers, porous nanofibers and surface rough nanotubes were prepared based on different water/oil phase separation processes due to distinctive properties of oils. The crystallinity and morphology of as-prepared nanomaterials were characterized by XRD and SEM, the optical absorption property was analyzed by UV–Visual spectrophotometer, N_2 adsorption–desorption was carried to measure the micro-structures and pores distribution of obtained nanomaterials. The photocatalytic activities of as fabricated nanostructures were evaluated by the degradation of Rhodamine B (RhB) under illumination of a xenon lamp as light source. The results indicated that the different nanostructure can be obtained easily by changing the types of oil added into electrospun precursor solutions, and photocatalytic studies indicated that almost all of samples prepared by oil added precursors showed improved photocatalytic activities compared with their traditional counterpart. Our systematic study in this work implied that emulsion electrospinning is a simple and feasible method to prepare nanomaterials with diverse morphologies, which can be used in fabricating other semiconductor-based nanomaterials.

1. Introduction

As the historic work made by Fujishima and Honda on UV light induced water cleavage using a TiO_2 photoanode in combination with a Pt counter electrode immersed in an aqueous electrolytic solution in 1972 [1], the photocatalytic activity of TiO_2 nanomaterials has drawn great attentions due to its unique properties, for instance, physical and chemical stability, non-toxicity, low-cost and environmental friendliness [2–5]. After decades of research and development, TiO_2 nanomaterials have been successfully used in extensive fields, such as waste water purification, solar energy conversion, sensing as well as supercapacitors, based on their bright promise in large scale industrial applications [6–13]. Particularly, waste water purification, driven by photocatalytic activity of TiO_2 nanomaterials under solar irradiation is one of the most vital and promising methods for solve the water pollution in the world.

However, the practical broad applications of TiO_2 nanomaterials were greatly limited, on the one hand, due to the large energy gap (Eg) between conduction band (CB) and valence band (VB) of TiO_2 (Eg for anatase is 3.2 eV and Eg for rutile is 3.0 eV), the TiO_2 nanomaterials can only be excited by UV light irradiation. On the other hand, the relative slow mobility rate of photo-generated electrons and holes in TiO_2 nanomaterials increased their recombination during their transfer to surface, which leads to low quantum efficiency of TiO_2 nanomaterials. In order to overcome aforementioned shortcomings, numerous effective works have been made and lots of strategies have been proposed. One of the most attractive strategies is promoting the response of TiO_2 nanomaterials for visible light by decreasing energy band gap and broadening light absorption band. Another effective strategy is improving the separation of photo-generated electron–hole pairs excited in TiO_2 nanomaterials. The specific methods included metals/non-metals doping, noble metals doping, dye sensitization, and fabricating TiO_2 nanomaterials with high specific surface areas. Lots of

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technologies for fabricating these nanomaterials have been developed, including Sol–Gel, chemical vapor deposition (CVD), hydrothermal process and electrospinning etc. [14–19]. Particularly, electrospinning attracts much more attention due to its prominent advantages in fabricating one-dimensional nanomaterials, such as nanofibers, nanotubes and nanowires, with large aspect ratio, high carrier mobility rate and uniform morphology [20–25]. Under most circumstances, however, nanomaterials with unique morphologies, for instance, porous and tubular nanostructures or even the combination of these two are extremely expected because of their universal applications in solar cell, photocatalysis, and electrode materials due to their high specific surface areas [20], and the rough surface and porous morphologies of nanomaterials are in favor of improving the separation of photo-generated charge carriers due to the effect of surface dangling bonds and defects, which could serve as electron traps, formed in these nanomaterials with unique morphologies. Therefore, preparing nanomaterials with unique morphologies and high specific surface areas is of great significance in practical applications.

In 2002, I. G. Loscertales et al. fabricated monodisperse capsules with diameters varying between 10 and 0.15 micrometers based on phase separation effect [26]. After that, lots of works have been down by A.L. Yarin et al. and other groups in fabricating coaxial nanofibers by the combination of electrospinning method and water/oil phase separation effect, which they named as emulsion electrospinning [27–31]. Recently, Lu et al. fabricated porous TiO_2 nanotubes with high photocatalytic activity by emulsion electrospinning method [3], our team also prepared porous SnO_2/TiO_2 nanofibers with high photocatalytic degradation efficiency of RhB in previous work [32]. While, as best knowledge as we known, the effect of oil added in precursor on morphologies of products and the feasibility of this method have not been systematically studied yet.

In this work, we systematically studied the effect of different oil on morphologies of emulsion electrospun products by changing the type of oil added in precursors for electrospinning, and TiO_2 nanomaterials with diverse morphologies, including, nanoparticles, necklace-like nanofibers, porous nanofibers and rough surface nanotubes were prepared. The photo-degradation of RhB was carried to evaluate the photocatalytic activity of as-fabricated nanomaterials as one of their potential applications. The results indicated that the TiO_2 rough surface nanotubes demonstrated the highest degradation rate due to their largest surface-to-volume ratio, and almost all of samples derived from precursors with oil showed improved photocatalysis compared with that of solid TiO_2 nanofibers fabricated by traditional electrospinning method. The circulating experiments and investigation on degrading of MB and phenol indicated the good stabilities and versatilities of all samples. Our results indicated that emulsion electrospinning is a simple, reliable and feasible method to prepare nanomaterials with diverse morphologies and micro-structures, due to different water/oil phase separation process directly related to distinctive properties of oils. The work we made here paved the way to fabricate nanomaterials with varieties of morphologies and micro-structures in a simple and convenient way for their potential applications in photocatalysis, solar cell, supercapacitors and energy conversion etc.

2. Experimental

2.1. Materials and methods

The chemical reagents with analytical grade were purchased from Lanzhou Zhongke Kate Equipment Distribution Co. LTD (Lanzhou, China) and used without further purification unless otherwise stated. Polyvinylpyrrolidone (PVP, Mw = 1,300,000) was purchased from Sigma–Aldrich Chemical Inc. Plant oil (Model Number: 0085927522) was purchased from Tongda Oil Processing Co. LTD (Lanzhou, China), gasoline and diesel were purchased from gas station of Lanzhou, China, mechanical pump oil was provided by China national petroleum Co. LTD (Lanzhou, China), and the castor oil was purchased from Baishi chemical Co. LTD (Tianjin, China). Deionized water was used in whole experiments and all of the experiments were employed at room temperature (RT) under ambient environment.

In a typical way, 2.0 g of tetrabutyl titanate ($C_{16}H_{36}O_4Ti$) was mixed with 3 ml of ethanol, 1 ml of acetic acid, stirred vigorously for about 40 min until light yellow solution formed, marked as Solution 1 (S1). And 1.0 g of PVP was dissolved in 4.5 ml of N,N-dimethylformamide (DMF) and 2 ml of ethanol and stirred vigorously for 30 min to form homogeneous transparent solution with specific viscosity marked as Solution 2 (S2). And then, 2 ml of plant oil was added into mixture of S1 and S2, as long as the mixture was stirred vigorously for more than 12 h, and defined as precursor with plant oil for emulsion electrospinning (PWP), other precursors including different kinds of oils were prepared by similar processes to that of PWP, and defined as precursor with gasoline (PWG), precursor with castor oil (PWC), precursor with diesel (PWD), precursor with mechanical pump oil (PWM), according to the different kind of oil was added into solutions, respectively. The precursor without oil (PWO) was also prepared as a reference. The electrospinning experimental system contains a glass syringe with a metal spinneret (inner diameter of 0.5 mm) and a collector made by stainless steel, the temperature of collector keeps at 80 °C controlled by an electric hot plate. A DC of 16 kV was applied between spinneret tip and collector with distance of 15 cm, the flow rate was controlled by gravity and electrostatic force. After electrospinning, the as-spun nanofibers were placed in electric thermostatic drying oven at 60 °C for more than 24 h for slow phase separation between remained solvents and oil. Then the as spun materials were sent into a furnace and annealed at 500 °C in air for 2 h with the heating rate of 5 °C per min, after naturally cooling down to RT, the TiO_2 nanomaterials with different morphologies were obtained, the labels of different annealed products were defined as same as the precursors for the sake of consistency, such as the final electrospun products derived from precursor PWO was labeled as sample PWO.

2.2. Characterizations of materials

The morphology of the obtained materials was characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4800), the crystal structure of materials was measured by grazing-angle X-ray diffraction (XRD, Philips, X'Pert Pro, Cu-Ka1, 1.54056 A). N_2 absorption–desorption measurement was conducted on a Tristar II 3020 Specific Surface Area and Pore Size Analyzer at 77 K for analysis of the surface structure and pores distribution of all obtained materials. The optical absorption spectrum of materials was measured by Zolix Omni DRASFluo Integrated photoelectric spectrometer with an integrating sphere.

2.3. Photocatalytic test

Before the measurements, 50 mg solid photocatalyst was put into 100 ml of RhB solution with an initial concentration of 20 mg/L. After stirred in the dark for 30 min to obtain a good dispersion and establish adsorption–desorption equilibrium between the organic molecules and photocatalysts, the mixture solution was put in a home-made photo-reactor with a xenon lamb with power of 350 W as the light source, and there was no any filters were set between the light source and sample during whole experimental processes. The whole system was set in a closed box for eliminating the light