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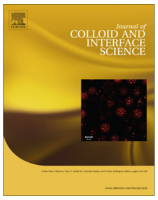

Enhanced visible-light photocatalytic performance of electrospun carbon-doped TiO_2/halloysite nanotube hybrid nanofibers

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ABSTRACT

In this work, the effects of halloysite nanotubes (HNTs) on the visible-light photocatalytic ability of electrospun carbon doped TiO_2/HNT (C—TH) nanofibers have been explored. Structural and morphological investigations demonstrate that incorporation of HNTs into anatase C—TH hybrid nanofibers was easily achieved by using sol–gel processing combined with electrospinning approach, thus HNTs could be uniformly embedded in the electrospun nanofibers. The visible-light photocatalytic efficiency of C—TH hybrid on the degradation of methyl blue (MB) was greatly enhanced with the combination of moderate amount of HNTs (8%), which was 23 times higher than that of commercial anatase TiO_2. Mechanism of the enhancing effect of HNTs has been explored by analyzing the dual-effect of adsorption and photocatalysis in various amounts of HNTs incorporated C—TiO_2 nanofibers. With nanotubular structure and considerable adsorption ability, incorporated HNTs functioned as porogen agent in C—TH nanofibers. This simple incorporation approach increases the specific surface areas of nanofibers, which improves the mass transport of reactant into the nanofibers and the adsorption of visible-light by scattering, meanwhile may suppress the charge recombination and enhance photoinduced charge separation, thus efficiently enhancing visible-light photocatalytic performance of the C—TH hybrid nanofibers.

1. Introduction

Currently, it is highly desirable to develop advanced materials being capable of exploiting clean and renewable solar energy for solving the environmental pollution problems, meanwhile saving energy resources in our planet earth [1–3]. Titanium dioxide (TiO_2) is one of the most promising semiconductor photocatalyst for the chemical utilization of solar energy, which has found world-wide applications in many fields including water/air pollution abatement [4–6]. As is known to all, the photocatalytic property of TiO_2 is derived from the interaction between electron–hole pair (e^-h^+) and molecules close to the photo-excited active centers in catalyst surface. However, the exciton of e^-h^+ pair in pure TiO_2 could only be achieved by ultraviolet (UV) light ($\lambda < 420$ nm) irradiation because of the high band gap energy of TiO_2. Thus, high visible-light (Vis) photocatalytic efficiency of TiO_2 based material mainly relies on a relatively narrower band gap (<3.2 eV for anatase, and <3.0 eV for rutile). In addition, for a fast diffusion of pollutant and an effective utilization of visible-light, materials with high specific surface area are also favorable [7–10].

There are many reports about the composites of TiO_2 and carbonaceous materials for Vis-photocatalysts, which have significantly improved the photocatalytic performance of TiO_2 [11–13]. With impurity states nearing the valence band edge and inhibiting recombination of e^-h^+ pair, doping of carbon atoms or carbonate species could narrow the band gap of TiO_2 and shift the absorption edge to the visible light region [12,14]. Hybridizing TiO_2 with conjugated structural materials including graphene and carbon nanotubes could lower the band gap and act as a visible-light sensitizer during an interfacial charge transfer process [15,16]. Except for the carbon sensitization, other factors such as phase type, thickness of coating-layer [17], morphologies [18] and oxygen vacancy concentration [19] also play important roles in the photocatalytic degradation process. It has been reported that the diffusion path of dye molecule could be increased by loaded carbon via its dye adsorption ability. However, the carbon coating layer decreases the light intensity irradiated on TiO_2 thus degrades the catalytic activity [20]. Hollow microsphere structural carbon modified TiO_2 (CTHS-500) with high surface area and carbon doping amount exhibits a superior visible-light photocatalytic activity for the degradation of toluene than that of CTHS-400 and CTHS-600, which are annealed at different temperatures [21]. Hence, a well-designed and synergistic architecture of TiO_2 based hybrids is important for the advanced photocatalytic performance.

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Electrospinning, a simple and versatile technique for the fabrication of one-dimensional (1D) structural fibers, has recently been reported to be advantageous in the separation of e^-h^+ pairs by the vectorial transport of photogenerated charge carriers through the grain boundaries of TiO_2 nanofibers [22]. Furthermore, electrospun TiO_2 nanofibers gain the benefit of recyclability and are free of secondary pollution during the practical applications compared with TiO_2 nanopower. Halloysite ($Al_2Si_2O_5(OH)_4{\cdot}2H_2O$) nanotubes (HNTs) is a type of natural clay with nanotubular structure formed by rolling layers of tetrahedral sheets of silica as outer surface and octahedral sheets of alumina as lumen surface. Growing attention has been attracted on HNTs during recent years due to their excellent adsorption capacity, mechanical property, biocompatibility, unique surface chemical state and cost-effectiveness [23–26]. Several reports have demonstrated that a thin coating of Al_2O_3 or SiO_2 on nanocrystalline TiO_2 films could function as physical barrier for both electron injection and charge recombination reactions in dye sensitized solar cells [27,28]. These work inspired us that halloysites with similar chemical composition would be promising candidates to improve the photocatalytic performance of TiO_2. Besides, many reports have investigated the effects of halloysites in electrospun polymer nanofibers as drug-delivery vehicle for encapsulation and release of drugs [29,30], which demonstrated a good prospect and feasibility of the combination of HNTs and electrospinning.

Herein, we report the fabrication of carbon doped TiO_2/HNT (C—TH) hybrid nanofibers by one-pot electrospinning. The performance of halloysites incorporated composites on the photocatalytic degradation of methyl blue (MB) under visible-light is studied. The enhancing mechanism of HNTs on the catalytic performance and the factors influencing the photocatalytic activity of the C—TH hybrids are discussed.

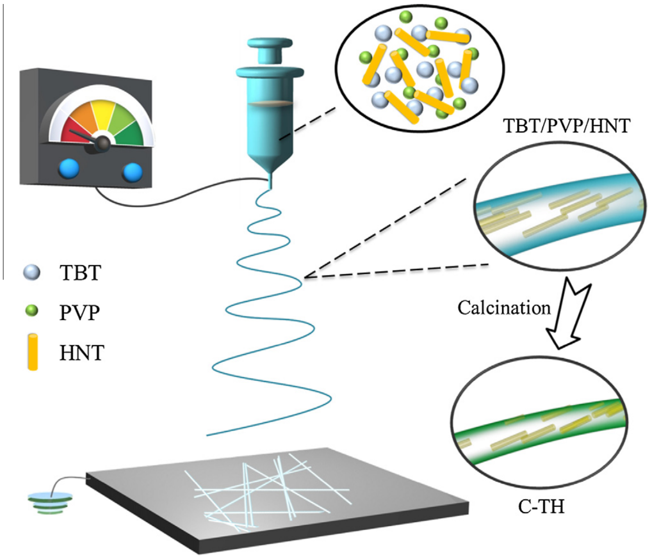
2. Experimental section

2.1. Materials

Halloysite nanotubes were obtained from Zhengzhou Jinyangguang China Clays Co., Ltd. (China). Poly(vinyl pyrrolidone) (PVP, Mw = 1,300,000) and titanium butoxide (TBT) were purchased from Aladdin Chemical Reagent Co. Ltd. Ethanol and acetic acid were supplied by Sinopharm Chemical Reagent Co., Ltd. All of the reagents were used as received without further purification. Commercial TiO_2 (Sinopharm Chemical Reagent) was used for the blank experiments.

2.2. Preparation of C—TH nanofibers

TBT was used as titanium precursor and PVP functioned as template and carbon source. Typically, 0.64 g TBT, 0.32 g PVP and 50 mg HNTs (mass ratio of TBT:HNTs = 100:8) were dispersed in a mixed solution of ethanol and acetic acid (weight ratio = 3:1), followed by magnetic stirring at ambient temperature for half an hour. Subsequently, the as-formed homogeneous precursor solution was transferred into a plastic syringe for electrospinning at a fixed electrical potential of 10 kV. The electrospinning solution was fed at a speed of 15 mL h^{-1} with a distance of 12 cm between the needle tip and the collector, forming a fiber membrane on a collector of aluminum foil. The electrospun nanofiber membrane were dried overnight at 60 °C to remove residual solvent, then calcined at 500 °C in a crucible covered with a cap under air atmosphere for 2.5 h to obtain C—TiO_2/8% HNT (C—TH-8) hybrid nanofibers (as shown in Scheme 1). By controlling the amount of HNTs, C—TiO_2/HNT hybrid nanofibers with 0%, 4% and 12% HNTs were obtained accordingly, which were abbreviated as C—T, C—TH-4, and C—TH-12, respectively.



Scheme 1. Schematic illustration of the synthesis of C—TH hybrid nanofibers.

2.3. Characterization

X-ray diffraction (XRD) measurements were conducted on a PANalytical X'Pro X-ray diffractometer (from Netherlands) with Cu Kα radiation (λ = 0.1542 nm) under a voltage of 40 kV and a current of 40 mA. The morphologies of the samples were investigated using a transmission electron microscope (TEM, Tecnai G2 20 TWIN, China) under an accelerating voltage of 200 kV and a field-emission scanning electron microscope (SEM, Ultra 55, Germany) at an acceleration voltage of 20 kV, where TEM samples were prepared by dropping the sample dispersion on the copper grids and dried in air. X-ray photoelectron spectroscopy (XPS) analyses were performed with a VG ESCALAB 220I-XL device (from America) to investigate the surface properties of the samples. All XPS spectra were corrected using C 1s line at 284.6 eV. Curve fitting and background subtraction were accomplished using XPS PEAK 41 software. All electrochemical measurements were performed using a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., China). Methylene blue concentrations were calibrated and determined by UV–vis spectrophotometer (Perkin–Elmer, Lambda 35, America) at a wavelength of 664 nm.

2.4. Evaluation of adsorption and photocatalytic activity

The photocatalytic degradation of MB was performed in a stirred quartz reactor filled with 50 mL MB aqueous solution (20 mg/L) and 10 mg of catalyst. The reactor was equipped with 50WUV lamps with short-wavelength components ($\lambda < 420$ nm) of the light that has been cut off by a glass optical filter. All of the photocatalytic experiments were carried out after the adsorption of MB in the dark for 60 min under stirring. Afterwards, the reactor was exposed to the visible-light irradiation under ambient conditions and rigorous stirring. At certain time intervals, 3 mL of sample solution was taken out during the experiments and centrifuged to remove the catalyst completely, then MB concentration was determined by UV–vis spectrophotometer. For the evaluation of adsorption ability, MB adsorption experiments were carried out in the dark with the same procedure as the photocatalytic experiments described above. The removal percentage by adsorption or