Separation and Purification Technology 168 (2016) 284–293

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Graphene wrapped porous tubular rutile TiO_2 nanofibers with superior interfacial contact for highly efficient photocatalytic performance for water treatment

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ARTICLE INFO

Article history:
Received 18 June 2015
Received in revised form 1 March 2016
Accepted 31 May 2016
Available online 1 June 2016

Keywords:
Nanofiber
Mesoporous
TiO_2
Wrapping
Composite
Photocatalytic activity

ABSTRACT

Reduced graphene oxide (rGO) wrapped tubular and porous rutile TiO_2 nanofibers were synthesized by electrospinning together with the help of easy chemical methods. Controlled electrospinning produced pores (30–60) nm on the side walls of the tubular nanofibers. Structural and morphological results demonstrate the success of wrapping by rGO. The specific surface area measurement revealed a high surface area of 232.3 $m^2 g^{-1}$ for the composite nanofibers. Control over the composition of the composites leads to an efficient photogenerated charge carrier separation and reduced electron-hole recombination rate. As a result, the photocatalytic activity of the composites was enhanced compare to bare porous tubular nanofibers (PTNF). Subsequently, the photocatalytic activity of the composites enhanced greatly compare to only TNFs due to porous and tubular structures of the nanofibers and also to the high surface area of rGO.

1. Introduction

TiO_2, a typical semiconductor photocatalyst, has stimulated great interest in recent years due to growing environmental concerns, energy demands, high photocatalytic performance, strong photo oxidation power, long term stability, photodurability, chemical and biological inertness, mechanical robustness and non toxicity [1,2]. The electronic and optical properties of TiO_2 nanostructures depend on their size, structure and crystal types [3]. Rutile structure has better chemical stability, higher refractive index and high dielectric constant among the various polymorphs of TiO_2. Moreover, surface chemistry of crystalline rutile nanoparticles has been intensively explored, as their chemical activity greatly depends on surface structures [4,5]. Calcination at high temperatures leads to agglomeration and growth of the nanocrystalline particles, resulting in the decrease of surface area and leading to poor photocatalytic performances in rutile phase [6,7]. However, rutile has been found to be more active for photocatalysis than anatase [8]. Introduction of porosity with a hollow structure in rutile phase can lead to enhancement of the performance, because of their ability to interact with atoms, ions, and molecules with high surface area. Hence, such unique properties considerably beneficial for the evolution of chemical and electronic acreage to offer new opportunities in the field of catalysis, electronic devices, and drug delivery systems [9,10]. Recently, porous and hollow structured materials have played a crucial role in the biological drug delivery, photocatalytic degradation of organic waste, and photon energy conversion [11]. More currently, hollow structure with micro porous crystalline shells have attracted research interest because they have large storage capacities as well as provide a convenient environment for the accommodation of various guest species to pass easily into their internal cavities [12,13]. Thereby, the presence of hollow and pores with one dimensional TiO_2 nanofibers can greatly promote their physical and chemical properties which lead to enhancement of the capability of dye loading and pollutant adsorption [14]. The application of TiO_2 is hampered by their intrinsic disadvantages such as wide band gap (rutile ~3.0 eV) and short charge recombination time ($\sim 10^{-9}$ s) compared to the chemical interaction time ($\sim 10^{-3}$ to 10^{-8} s) with the adsorbed dyes or other molecules on the surface of TiO_2 [15,16]. Several attempts have been made to overcome this problem such as doping, metal deposition, surface sensitization, coupling with semiconductors and composite materials of TiO_2 with various carbon materials such as activated carbon and carbon nanotubes

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http://dx.doi.org/10.1016/j.seppur.2016.05.059
1383-5866/

(CNTs) [17,18]. Among the carbon family, Graphene has shown great interest due to its unique electrical and mechanical properties which could be an ideal mechanical support and good interfacial contact with adsorbents and electric charge carrier transporter to construct nanocomposites with enhanced performances [19]. The TiO_2/graphene composite has emerged as an attractive photocatalyst that can enhance the photocatalytic activity of TiO_2 material [20]. Nevertheless, when TiO_2 nanostructures are incorporated into graphene instead of uniformed distribution they form agglomeration, which dramatically reduces the synergetic catalytic effect of TiO_2 nanostructures and graphene. Meanwhile the synthesis of graphene wrapped semiconductor nanostructure is a novel and a new technique to overcome the problem of agglomeration and to obtain efficient photogenerated charge carrier separation across the interface. In our previous work, we already demonstrated the potential of reduced graphene oxide (rGO) wrapped anatase TiO_2 nanofibers in the photodegradation of organic wastes [21].

In the present work, the fabrication of rGO wrapped porous tubular TiO_2 nanofibers (PTNFs) in rutile phase with high surface area and superior photocatalytic performance has been discussed. Electrospinning technique was adopted for the synthesis of PTNFs. These synthesized PTNFs showed enhanced photocatalytic property compared to previously reported photocatalytic performances of TiO_2 in rutile phase. It is worth emphasizing that, wrapping of rGO over these PTNFs in rutile phase was achieved by simple hot plate drying and then, the reduction of GO was performed by annealing without using any hazardous chemicals. Structural and morphological characterization provides the evidence of uniform and homogeneous wrapping of rGO over the porous tubular rutile TiO_2 nanofibers. This uniform wrapping leads to efficient charge separation of photogenerated electron-hole pair across the interface of PTNFs/rGO and further enhances the photocatalytic efficiency of these PTNFs.

2. Experimental

2.1. Materials

Analytical grade of commercial graphite powder (99.95%), titanium tetra isopropoxide $Ti\{COH(CH_3)_2\}_4$ (97%), and polyvinylpyrrolidone (PVP) (Sigma-Aldrich, Mw = 13,00,000), N, N-dimethylformamide (DMF), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$, 98%), sulfuric acid (H_2SO_4, 98%), methyl orange (MO), and absolute ethanol were used without any further treatments or additives.

2.2. Fabrication of PTNFs

In a typical electrospinning process [21], the spun solution was prepared in two steps. Initially, titanium tetra isopropoxide was dissolved in the mixed solution of ethanol and acetic acid. The mixed solution was stirred for an hour to obtain a transparent yellow solution. The second solution was prepared using a mixture of 10 ml of ethanol and 2 ml of N,N-Dimethylformamide (DMF) mixed with half a gram of polyvinylpyrrolidone (PVP) to control the viscosity under the magnetic stirring for 30 min. The above prepared solution was added to this solution and stirred for further 10 min. The obtained viscous transparent solutions were loaded separately into a 2-ml syringe with a stainless steel needle of 0.6 mm inner diameter which was then used to maintain a constant flow rate of 0.3 ml/h using a syringe pump. Electrically grounded aluminum foil was used as the collector. The distance between the tip of the needle and the aluminum foil was maintained at 15 cm and a DC voltage of 20 kV was applied. The charged nanofibers were deposited on the metal collector. To obtain rutile TiO_2 nanofibers, the obtained fibers after electrospinning were calcined in air at 800 °C for 1 h.

2.3. Fabrication of PTNFs/rGO composites

Graphite oxide (GO) was synthesized from natural graphite powder using Hummer's method [22]. Initially, 1.25 mg, 2 mg and 5 mg of graphite oxide were added separately into 60 ml of deionized water under sonication for 1 h to obtain a homogeneous dispersions of GO. Further, 5 mg of PTNFs was added separately into each of the GO solutions under constant stirring at room temperature to obtain a homogeneous mixture. Finally, the resulting brown colored sample was collected and annealed at 400 °C for 1 h in an Argon atmosphere in order to reduce the GO sheets to form rGO wrapped PTNFs in a weight ratio of 1:0.25, 1:0.5, 1:1 for TiO_2:GO, which will be referred as PTNFG-1, PTNFG-2 and PTNFG-3 respectively.

2.4. Characterization techniques

The morphology and microstructures of the samples were examined using a Hitachi SU8000 field emission scanning electron microscope (FESEM) and a high resolution transmission electron microscope (JEOL JEM 2100) operating at 200 kV. The crystalline structure was characterized using a Rigaku Rintz Ultima X-ray diffraction analyzer. Raman spectra were recorded at room temperature using a Horiba Jobin Yvon instrument with a 514-nm green laser as the excitation light source. Fourier transform infrared (FT-IR) spectral analysis was carried out using Nicolet FT-IR 4700 model with KBr pellets in the frequency range of 4000–400 cm^{-1}. The presence of the element in the composite material was analyzed by X-ray photoelectron spectroscopy recorded on Theta Probe-Thermo Fisher scientific Inc X-ray photoelectron spectrometer. The specific surface area and pore volumes were analyzed by studying the N_2 adsorption-desorption isotherms as obtained from Quantachrome autosorb iQ2 automated gas sorption analyzer. Photoluminescence (PL) spectrum was acquired using a Horiba Jobin-Yvon spectrometer with He–Cd laser. Thermal properties of samples were analyzed by thermogravimetry (TG) measurements using SII EXSTAR 6000 with a TG/DTA 6200 thermogravimetric analyzer from room temperature to 1000 °C with sealed platinum pans under Ar flow.

2.5. Photocatalytic measurements

Methyl Orange (MO) was used as an organic pollutant to evaluate the photocatalytic activity of the samples in an aqueous medium under UV irradiation. For UV irradiation, the quartz reaction tube was placed axially and clamped in front of a single UV lamp (power: 20 W, emission wavelength: 365 nm). The distance between the lamp and the quartz tube was maintained at 10 cm. 0.01 g of each sample was added to 25 ml of the MO solution at 10 mg (MO)/L. Prior to illumination, the suspension was magnetically stirred and sonicated for 20 min in darkness to achieve adsorption–desorption equilibrium of the dye on the surface of the photocatalyst. It was then irradiated with ultraviolet light. At time intervals of 15 min, 3-ml aliquots were sampled and filtered through a 0.22-μm PTFE filter to remove the catalyst. The filtered solutions were analyzed by an UV/VIS spectrometer (model: V-570) and the absorbance spectra of MO (major absorption band at approx. 462 nm) was recorded to measure the change in concentration of MO, since the intensity of the absorption band at ~462 nm is closely proportional to the concentration of MO.