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Direct synthesis of novel vanadium oxide embedded porous carbon nanofiber decorated with iron nanoparticles as a low-cost and highly efficient visible-light-driven photocatalyst

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ABSTRACT

Template-free porous carbon nanofibers embedded by vanadium oxide and decorated with iron nanoparticles (Fe@V-CNF) were prepared in a time and cost-saving manner by combining electrospinning and heat treatment processes. Cost-saving ammonium metavanadate was used as a semiconductor precursor of vanadium oxide (VO_x) as well as porogen. The generated pores in the carbon nanofiber (CNFs) matrix formed pathways between the embedded VO_x and the surface of CNFs and Fe NPs, thus, facilitate photogenerated electron transfer. The characterization results revealed that Fe@V-CNF comprised graphitic fibers with well-dispersed distribution of nanosized Fe NPs (~7 nm) along the surface of CNF. Thereby, it enhanced the visible-light harvesting. The prepared Fe@V-CNF had remarkable light absorption in the visible region. It demonstrated much higher photocatalytic efficiency of photodegradation of organic dyes compared with the pure CNF and vanadium oxide embedded CNF (V-CNF). Notably, Fe@V-CNF achieved 99.9% dye degradation within 15–20 min. And, it could be conveniently recycled due to its one-dimensional nanostructural property.

1. Introduction

Since the demonstration by Honda and Fujishima of the photoelectrolysis of water using a TiO_2 electrode under an anodic bias potential [1], intensive research efforts have been devoted to the development of photocatalytic materials, with the aim of utilizing solar energy and thus addressing the increasing global concerns of environmental remediation and clean fuel production [2]. Nanostructural semiconductor metal oxides can degrade various organic pollutants under UV light irradiation. Therefore, different kinds of nanostructured semiconductor metal oxide photocatalyst, such as Bi_2O_3, Fe_2O_3, TiO_2, ZnO, and so forth, have been developed for creating a convenient environment for human beings [3]. Interestingly, vanadium oxides have been widely used as the catalyst with band gap around 2.6 eV [4]. Such a narrow band gap could makes it active in a wide region of visible-light frequencies (<600 nm), which cover most of the solar light region. However, the rapid electron–hole pair recombination makes the vanadium oxide containing catalysts exhibit low activity in both ultraviolet light and visible-light [5]. To enhance the photocatalytic performance of catalysts, two approaches are frequently implemented: The first focuses on improving the separation efficiency of photogenerated carriers (photogenerated electrons and holes) by supporting appropriate co-catalysts (such as noble metals and metal oxides) [6,7] or constructing catalysts with various compositions [8,9]. The second centers on developing nanoscaled or porous photocatalysts with greatly enhanced surface areas, because the large surface area provides more active sites at which the photocatalytic reaction occurs, and nanoscaled materials shorten the distance that electrons and holes migrate from bulk to reaction active sites [10–13]. Thus, we expected that high-performance photocatalysts should be obtained when these two strategies are combined.

Recently, one-dimensional (1D) carbon–semiconductor hybrid materials have become a new class of photocatalysts, which has attracted a lot of attention [14,15]. The 1D structure not only provides shortened pathways for electron transport, but also remarkably facilitates the penetration of electrolyte from the direction perpendicular to the longitudinal axis of the fiber [16]. Among 1D materials, carbon nanofibers (CNFs) and carbon nanotubes (CNTs) are unique carbon materials characterized by nanoscale graphite-like structures that show outstanding electronic conductivity. Their wide visible-light absorption at a wavelength of 400–800 nm with high absorption of organic

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pollutants facilitate the interface reaction of photocatalysis [17][18]. The composites combine carbon and semiconductor photocatalysts, which could possibly offer desirable efficiency for separating electron–hole pairs [14]. Compared to other members in carbon nanomaterial family, mesoporous carbon nanofibers are characterized with higher specific surface area, pore volume and better gas permeability [15]. It gained great interest for broad applications ranging from adsorbent, separation, catalyst, energy storage and conversion, to biological uses [12]. Therefore, many studies have been focused on developing state-of-the-art porous carbon nanofibers (CNFs) to build new devices with improved properties [16]. However, only a few methods have been reported for the direct synthesis of porous CNFs by carbonization of 1D polymers [16]. Poly(acrylonitrile) (PAN) a well-known polymer with good stability and mechanical properties, has been widely used in producing carbon nanofibers (CNFs) [19]. The synthesis of porous CNFs with mesoporous channels (2–50 nm) and micropores (0–2 nm) using PAN has been reported by several groups [19,20], but most of these strategies still suffer from complicated selective extraction procedures [20]. Thus, it remains a great challenge, but of great desired to develop a template-free and economic method to conveniently synthesize porous carbon nanofibers with high surface area and large pore size for different electrochemical applications.

Furthermore, iron oxides, such as hematite (Fe_2O_3) and magnetite (Fe_3O_4) are abundant, inexpensive, and environmental friendly materials [21]. These iron oxides have been intensively investigated as gas sensors [22], electrodes [23], and photocatalysts [24]. Fe_2O_3 can absorb and utilize about 40% of the incident solar spectra because of its small band gap (approximately 2.2 eV) [25,26]. More importantly, different from the semiconductor characteristics of most metal oxides, Fe_3O_4 can be considered as a conductor because its conductivity is as high as 1.9×10^6 S m^{-1}. This high conductivity of Fe_3O_4 and CB level (1 V vs. NHE) makes it a good candidate for coupling with VO_x and improving photocatalytic performance by enhancing light harvesting and charge transport.

In this paper, we describe herein a new photocatalyst of 1D mesostructured VO_x embedded CNF membrane decorated with Fe NPs (Fe@V-CNF) by simple combination of electrospinning and heat treatment. The investigation of photocatalytic ability indicated that the as-prepared nanocomposites exhibited enhanced photocatalytic activity in the decomposition of MO, MG and RhB dyes under visible-light irradiation, which might be attributed to the light harvesting efficiency and separation efficiency of photogenerated carriers based on the photosynergistic effect among the three components of VO_x, carbon and Fe. What is more, the high specific surface area and high absorption of Fe@V-CNF could facilitate the interface reaction of photocatalysis. Furthermore, the Fe@V-CNF could be easily recycled without decrease in the photocatalytic activity due to the large length to diameter ratio of one-dimensional nanostructures.

2. Experimental section

2.1. Chemicals

Poly(acrylonitrile) (PAN, Mw = 150,000), poly-(vinylpyrrolidone) (PVP, Mw = 1,300,000) and ammonium metavanadate (NH_4VO_3) N,N-dimethylformamide (DMF), methyl orange (MO), malachite green (MG) and Rhodamine B (RB) were purchased from Aldrich Chemical Co. Iron nitrate ($Fe(No_3)_3 \cdot 9H_2O$) was provided by Sinopharm Chemical Reagent Company. All the above materials were used without further purification.

2.2. Synthesis of mesostructured Fe_3O_4 decorated mesoporous CNFs (Fe@V-CNF)

Inorganic ammonium metavanadate (NH_4VO_3) was used as a precursor, which is cost-saving and more suitable for industrial production. NH_4VO_3 could perform as a porogen agent in constructing the porous CNFs. It has been reported that the NH_4VO_3 decomposed at low temperature 200–280 °C and produce intermediate vanadyl compounds species (e.g. $(NH_4)_2V_6O_{16}$ and $NH_4V_4O_{10}$) before the formation of V_2O_5 at 450 °C [27]. Moreover, V_2O_5 has a melting point of 700 °C (2B1258, Junsei) which can be dissociated enough by heat treatment as metal and oxygen at a higher temperature than the m.p. of metal oxide. The dissociated oxygen in carbon fibers could form carbon monoxide and carbon dioxide during carbonization that would generate the pores structure. The PVP was chosen as a co-polymer with PAN for the following reasons: (1) the mixture of PVP and PAN has been reported to perform as a phase-separated polymer during the electrospinning, which could facilitate the decoration of CNFs with Fe NPs [28]. (2) PVP improves the spinnability of polymer mixture solution by reducing the viscosity and thereby decreases the diameter of the electrospun NFs.

In a typical one-boat synthesis, NH_4VO_3 solution was prepared by dissolving 0.1 g NH_4VO_3 in 9.0 g DMF at 80 °C for 3 h with vigorous stirring to form purple solution, then 1.0 g PAN was added with continued stirring at the same temperature for 2 h to form yellowish homogenous solution. Afterward, the solution was cooled down to the room temperature. $Fe(NO_3)_3$ solution was prepared by dissolving 0.05 g of $Fe(NO_3)_3$ in 9.0 g of DMF at the room temperature with vigorous stirring for 30 min followed by adding 1.0 g of PVP and kept under stirring for another 30 min. The two solutions were mixed and stirred at room temperature for 2 h. The above viscous brown solution was drawn into a hypodermic syringe for electrospinning. The positive voltage applied to the tip was 15 kV and the distance between the needle tip and the collector was 20 cm. A dense web of membrane fibers was collected on the aluminum foil. To be carbonized, the substrates were first placed in a tube furnace and stabilized in air for 4 h at 250 °C. Then they were subjected to nitrogen gas at 1000 °C at a ramp rate 5 °C/min, and finally they were cooled to the room temperature. The obtained carbon nanofiber denoted as Fe@V-CNF. Meanwhile, vanadium oxide embedded CNF was prepared by following the same method without adding $Fe(NO_3)_3$ and denoted as (V-CNF).

2.3. Characterization instruments and techniques

The scanning electron microscopy (SEM XL30, Philips, Netherlands) and transmission electron microscopy (TEM; high resolution TEM [HRTEM], JEM 2011, JEOL, Japan) were used to characterize the morphology of the products. X-ray diffraction (XRD) measurement was carried out using an X-ray diffractometer (D/MAX-rB, Rigaku, Japan). Ultraviolet–visible spectroscopy (UV–Vis) (UV-2450, Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS) was performed on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Ka radiation (hn = 1253.6 eV). Thermogravimetric analysis was conducted on thermogravimetric analyzer (TGA 2050, TA instruments) from 100 to 1050 °C with nitrogen flow rate (5 cm^3/min). Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore volume and pore size distributions were calculated using the Barret–Joyner–Halenda (BJH) model. The concentrations of metal ions were measured by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), (Optima 2100 DV, Perkin Elmer, USA).