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Full Length Article

Electrospun magnetic cobalt–carbon nanofiber composites with axis-sheath structure for efficient peroxymonosulfate activation

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ABSTRACT

Cobalt–carbon nanofiber composites (Co-CNFs) were synthesized by electrospinning and subsequent carbonization and their performance for peroxymonosulfate (PMS) activation was evaluated. Co-CNFs have a large aspect ratio (150 nm in diameter and several millimeters in length) to avoid aggregation and large specific surface area (1304 m^2/g) to provide more reaction sites for enhancing catalytic activities. Zero valence cobalt was proved to be the main cobalt species of axis or core of the fiber, which might account for its excellent magnetic response, and Co_3O_4 was the main cobalt species of sheath or coat according to XRD and XPS results. The Co-CNFs exhibited higher catalytic performances than Co_3O_4 or CNFs for PMS activation and dyes were completely removed in a short time in the Co-CNFs/PMS system. The Co-CNFs derived from cobalt acetate demonstrated the highest catalytic performance and their Co leaking was similar to that of catalysts derived from other cobalt salts. The degradation efficiency increased with the carbonization temperature, cobalt loading, degradation temperature, PMS and catalyst dosage. The dye degradation processes followed pseudo-first-order kinetics. The activation energy of Co-CNFs/PMS/orange G system was derived as 29.8 kJ/mol by the Arrhenius equation. The Co-CNFs exhibited high catalytic performances and excellent stability for five repetitive usage. The possible orange G degradation pathway was proposed based on intermediate detection.

1. Introduction

Sulfate radical-based decontamination technologies have attracted lots of attention recently as eco-friendly and cost-effective methods for treating non-biodegradable or refractory contaminants in wastewater [1]. Transition metal ions could activate peroxymonosulfate (PMS) to generate sulfate radicals and cobalt ion was proved to be the best catalyst activator [2]. Considering the difficulty in catalyst recycling and secondary contamination of homogeneous processes, the heterogeneous catalysts based on transition metal oxides have been extensively investigated [3]. These catalysts can be classified as mono-metal oxides (Co_xO_y, MnO_2) [4–6], bimetal oxides ($CoFe_2O_4$, $CoMn_2O_4$) [7,8], and supported metal oxides (Co_3O_4/Zeolites, Co_3O_4/graphene oxide) [9,10]. However, several challenges still exist for the practical application of these heterogeneous catalysts. For example, some nanomaterials usually tend to aggregate inevitably leading to the decrease of the catalytic activity [11,12] and some powder catalysts are difficult to separate from the treated water [13]. Since CNFs are readily available on a large scale, they can be easily separated and ameliorate the problems of other nanomaterials, such as aggregation, without functionalization, coating or decoration.

Carbon nanofibers (CNFs) are solid carbon fibers with lengths of a few micrometers and diameters of around 100 nm. CNFs have a relatively high specific surface area, large aspect ratio, high thermal and chemical stability [14,15]. The specific surface area of CNFs is reported up to 1877 m^2/g, which is among the highest ever reported for nanostructured materials [16]. CNFs have been widely applied in various environmental applications [17], such as photo-catalyst supports [18,19] and sorbents [20]. Nanofibers (NFs), the precursor of CNFs, can be fabricated via several approaches, such as the hydrothermal, sol-gel and electrospinning methods [21]. Comparatively, electrospinning technology is known to be the simplest and most inexpensive one from polymer solutions or melts to generate various fibers with diameters ranging from nanometers to micrometers. The electrospinning parameters can be altered to control the fiber morphology and chemical composition [22,23]. There are two routes for incorporating active species into electrospun NFs: using the NFs to absorb the species like a sponge or incorporating the species into the individual fibers as they are manufactured [24]. The first method exploits high adsorption ability of the NFs owing to their high specific surface area. The second one incorporates the substances into the electrospinning solution so that they are incorporated within the NFs. The active species should be dissolved

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or dispersed in the same solvents as the NF-forming polymer and the concentrations of the active species and polymer are limited.

In this study, catalysts for PMS activation were synthesized using the incorporating approach. Co-CNFs were synthesized by electrospinning organic solution containing cobalt precursor salt and polyacrylonitrile, followed by carbonization. Cobalt was incorporated into the fiber structure to minimize cobalt leaching and improve degradation efficiency. The catalysts were characterized using several techniques. Three organic dyes were selected as the probe compounds to test the catalyst performances since the dye concentration could be quickly analyzed by visible spectra or with the naked eyes. Furthermore, dyes are one group of pollutants that not only change the color of water but also adversely affect the eco-environment.

2. Materials and methods

2.1. Synthesis of the catalysts

The 8.0 wt% polyacrylonitrile (PAN, Mw 150000, Sigma-Aldrich, St. Louis, MO, USA) solution was prepared by dissolving PAN in N,N-dimethylformamide (DMF, TEDIA, Fairfield, OH, USA). Then, a certain amount of cobalt precursor ($CoSO_4$, $CoCO_3$, $Co(NO_3)_2$, $CoCl_2$ or $CoAc_2$) was added and the obtained mixture was stirred for 3 h to obtain homogeneous and transparent solution. Well-stirred solution was taken in a 5 mL glass syringe fitted with a metal needle of 0.8 mm inner diameter. The schematic of electrospinning setup is Fig. S1. The syringe was fixed horizontally on a syringe pump (NE-1000X, Farmingdale, NY, USA) with a feed rate 1 mL/h. A high voltage of 20 kV was applied using a DW-P303 high-voltage supplier (Dongwen, Tianjin, China). A grounded stainless steel plate collector was located at 15 cm from the end of the needle tip. The electrospun nanofibers (Co-PAN NFs) were collected on the collector and the fibers were dried for 24 h at room temperature after electrospinning processes.

Stabilization and carbonization of Co-PAN NFs were conducted in a GSL-1500X program control high-temperature furnace (Kejing Instrument Co., Hefei, China) to obtain Co-CNFs. Co-PAN NFs were stabilized by being heated up to 300 °C in air with ramp rate of 5 °C/min and stayed at this temperature for 1 h. Nanofibers were further carbonized by being heated up to 600, 800, 1000, or 1200 °C in an N_2 atmosphere at a rate of 2 °C/min and stayed at final temperature for 1 h. The obtained Co-CNFs cooled down to room temperature at the inert atmosphere. The resulting catalyst was labeled as X % Co-CNFs-Y Z °C, where X stands for the cobalt percent by weight (Calculated Values), Y represents the counter ion of cobalt precursor and Z denotes the carbonization temperature. The common used catalyst, 4% Co-CNFs-Ac 1000 °C, is abbreviated to Co-CNFs. Carbon nanofibers (CNFs) were also prepared using the same electrospinning, stabilization and carbonization processes without addition of cobalt salt for characteristic and catalysis comparison.

2.2. Characterization of the catalysts.

The texture and morphology of the Co-CNFs were investigated using a SU8000 scanning electron microscope (SEM, Hitachi, Tokyo, Japan). Co-PAN NFs were coated with a thin layer of gold by a JFC-1600 sputtering device (JEOL, Tokyo, Japan) prior to the S4800 SEM observation. The elemental composition and mapping were determined to investigate the distribution of Co in the Co-CNFs using a SEM coupling with energy dispersive X-ray spectroscopy (SEM-EDS, X-MAX^N, HORIBA, Fukuoka, Japan). Nitrogen adsorption-desorption isotherms were measured using an Autosorb-IQ-MP analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). The specific surface area was evaluated using the Brunauer–Emmett–Teller (BET) method and the pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) method. The crystallinity of the sample was studied by X-ray diffraction (XRD) performed on a PANalytical B.V XRD instrument (X pert pro MPD, Almelo, Holland), using filtered Cu Kα radiation with an accelerating voltage of 40 kV and current of 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the atom compositions and chemical states of materials using an ESCALAB 250Xi ESCA spectrometer (ThermoFisher, MA, USA). XPS analyses of the fresh Co-CNFs and in situ Ar ionic sputtered Co-CNFs were conducted on the Thermo ESCALAB 250Xi under 5×10^{-9} mbar, Al-Ka source (1486.6 eV). The analyzed area was 650 μm in diameter and the binding energies were calibrated by contaminated carbon (C1s at 284.8 eV). Ar ionic sputtering was performed under Monatomic Mode with a beam energy of 2 keV and a sputtering rate of about 10 nm min^{-1} for 0.5 min (1–1), 1 min (1–2), 3 min (1–3). Magnetic properties of the Co-CNFs were measured with a 7410-VSM vibration sample magnetometer (LakeShore, Westerville, OH, USA).

2.3. Evaluation of catalytic activity

The experiments were conducted in a series of 100 mL (final volume) aqueous solutions. The reactor was immersed in a water bath with a temperature controller (F-12, Julabo, Seelbach, Germany). A certain amount of dye (orange G (OG), methylene blue (MB), or Evans blue (EB)) was added to the solutions and stirred constantly to achieve equilibrium. The phosphate salts at various molar ratios were used as the buffer species for pH adjustment and the initial concentration was fixed at 0.1 mol/L. The catalysts were then added to the solutions. Finally, the oxidant PMS (Alfa Aesar, Ward Hill, MA, USA) was introduced to initiate the oxidation reaction. Aliquots were periodically taken away from the reaction solutions for following analysis. The solids were removed from the samples using disposable syringe filters or a magnet. The dye concentration was measured using a UV-2600 spectrophotometer (Shimadzu, Kyoto, Japan). The concentration of cobalt ions in solution leaching from the catalysts was measured using an ULTIMA inductively coupled plasma mass spectrometer (NexION 300X, PerkinElmer, Waltham, MA, USA). Experiments were performed in duplicate, and averages are reported with relative standard deviations indicated as error bars.

2.4. Degradation intermediate analysis

The degradation intermediates were analyzed using a Shimadzu 8040 liquid chromatography-mass spectrometer (LC-MS, Kyoto, Japan). A WondaSil C18-WR column (5 μm, 4.6 mm × 250 mm, GL Sciences Inc., Kyoto, Japan) was used to separate OG and the intermediates. HPLC grade methanol and water (20 mmol/L ammonium acetate) were used as mobile phase and the flow rate was set at 1.0 mL/min. The gradient program was as follows: started at 50% methanol and kept for 5 min, increased to 100% in 3 min then kept 12 min. The mass spectrometric measurements were carried out using an ESI or APCI in both positive and negative ion mode. ESI acted as an ion source with a voltage of 4 kV. DL and heat block temperature was 250 °C and 400 °C. CID gas pressure was 230 kPa. Nebulizing gas and drying gas flow was 3 L/min and 15 L/min, respectively. MS data was obtained by scanning from *m/z* of 20 to *m/z* of 500. The injection volume of sample was set at 10 μL.

3. Results and discussion

3.1. Characterization of the catalysts

The electrospinning parameters (such as applied voltage, needle-target distance, feed rate, ambient conditions) were optimized to get satisfied morphology and structure of the Co-PAN NFs as shown in Fig. 1A. It could be observed that the Co-PAN NFs with smooth surface were randomly distributed due to the bending instability of the electrospinning jet. The diameters of the NFs were relatively uniform with the values around 150 nm and the lengths could reach several