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3D-hierarchically structured Co_3O_4/graphene hydrogel for catalytic oxidation of Orange II solutions by activation of peroxymonosulfate

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ABSTRACT

We report a 3D-hierarchically Co_3O_4/graphene hydrogel (CGH) composite as a catalyst activator of peroxymonosulfate (PMS) for sulfate radical-based degradation of Orange II in a heterogeneous system. The physicochemical performance of the composite is analyzed by X-ray diffraction spectra, scanning electron microscopy, Raman spectroscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The results demonstrate that the samples are prepared resoundingly. The CGH hybrid composite completely removes Orange II wastewater within 6 min; furthermore, after five runs, the catalyst activity remains essentially unchanged and the macrostructure is followed consistently. This unusual macrostructure hydrogel of supported cobalt oxide indicates a high feasibility of commercial promotion to remove the azo dye.

1. Introduction

Azo dyes are diffusely implemented in various industries; non-biodegradability, toxicity and potential carcinogenic qualities of dyes have attracted a lot of attention [1,2]. Several techniques have been researched, such as physical adsorption, advanced oxidation processes (AOPs), biological treatment or photocatalysis. Between these methods, AOPs are a mild condition, simple operation, highly efficient, and environmentally friendly approach to the degradation of dye wastewater [3-5]. Peroxymonosulfate (PMS) is widely used in AOPs, and can generate a highly active radical, such as $SO_4^{-}\bullet$ [6,7]. It provides a higher oxidative potential (2.5–3.1 V) than other active radicals, which can increase the degradation rate, reveal a formidable oxidation ability and fully mineralize organic contaminants into H_2O and CO_2, etc. [8-11]. The combination of PMS and transition metal ions, such as Cu^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+}, can accelerate the generation of $SO_4^{-}\bullet$; Cobalt ions coupled with PMS have demonstrated optimum activation performance [12]. However, Co^{2+} may result in metal contamination and metal poisoning, caused by cobalt leaching in homogeneous systems [1]. In the present research, cobalt ions in the shape of Co_3O_4 loaded on graphene were shown to reduce cobalt leaching and increase the performance of degradation [13]. Three-dimensional (3D) graphene hydrogel with sp^2-hybridized carbon material has exhibited large surface area, high electrical conductivity and excellent mechanical strength [14]. Compared with powder material, 3D hydrogel material has higher activity and recovery as a consequence of a larger specific surface area from the self-assembly of nanomaterials into 3D macrostructures [15-18]. Wu et al. [19] reported that the combination of Fe_3O_4 nanoparticles with a 3D graphene aerogel showed an excellent ORR performance because of the high specific surface area and better durability than commercial Pt/C catalysts. Xu et al. [20] showed that the 3D graphene/$Ni(OH)_2$ composite hydrogel expressed a high specific capacitance and remarkable cycling stability. Cong et al. [21] reported that graphene/α-FeOOH and magnetic graphene/Fe_3O_4 hydrogels were synthesized by ferrous ions reduction of GO and *in situ* simultaneous deposition of nanoparticles on graphene sheets; the functional graphene-based hydrogels exhibit a robust capability for the removal of pollutants in water. Wang et al. [22] found that Co_3O_4 loaded onto graphene sheets and the catalytic performance was much higher than pure Co_3O_4, as the graphene played an active role in Co_3O_4 dispersion and pollutant degradation. However, to the best of our knowledge, few technologies to compound 3D-hierarchically structured Co_3O_4/graphene hydrogels have been applied to the degradation of dye wastewater. In this study, a green hydrothermal route is provided to compound 3D Co_3O_4/graphene hydrogels with a macrostructure as efficient heterogeneous catalysts activator of PMS for Orange II removal. The composite catalyst exhibits high catalytic activity, prominent long-term stability and excellent recovery for the activation of PMS to decompose Orange II.

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2. Experimental

2.1. Materials and chemicals

Natural graphite (300 mesh, 99.99%), potassium persulfate ($K_2S_2O_8$), phosphorus pentoxide (P_2O_5) and glycol [$(CH_2OH)_2$] were obtained from Aladdin Industrial Corporation. Potassium peroxymonosulfate (PMS), available as a triple salt of sulfate commercially known as oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, 4.5% to 4.9% active oxygen), was obtained from Shanghai Ansin Chemical Co. Ltd. and used as an oxidant. Other reagents including cobalt acetate [$Co(CH_3COO)_2{\cdot}4H_2O$], sulfuric acid ($H_2SO_4 \geq 98\%$), methanol ($CH_3OH$), sodium bicarbonate ($NaHCO_3$), absolute ethanol ($CH_3CH_2OH$), potassium permanganate ($KMnO_4$), hydrogen peroxide (30% H_2O_2) and hydrochloric acid (HCl 36%–38%) were supplied by Sinopharm Chemical Reagent Co. Ltd. (China).

2.2. Synthesis of materials

CGH: GO was prepared by oxidation of natural powdered flake graphite with the modified Hummers methods [23]. An aqueous suspension of GO (7.5 mg/mL) was prepared by adding 150 mg GO into 20 mL deionized water. The GO suspension and glycol (5 mL) were mixed by ultrasonication for 0.5 h and the slurry was stirred for 0.5 h 5 mL $Co(CH_3COO)_2{\cdot}4H_2O$ (116 mg/mL) aqueous solution was added into suspension slowly and stirred for 1 h Then the mixture was taken to an autoclave and heated at 453 K for 20 h. After cooling to room temperature, the resultant products were immersed in water for 1 h to obtain the hydrogel. Then the products were frozen overnight to maintain the morphology. Finally, the products were freeze-dried for 36 h to get the CGH composite catalysts.

Co_3O_4 and GH: Pure Co_3O_4 was prepared without an aqueous suspension of GO and graphene hydrogel (GH) was prepared without adding $Co(CH_3COO)_2{\cdot}4H_2O$; Other steps and conditions were the same as before.

CGP: Graphene was prepared by a surfactant-assisted liquid-phase exfoliation process [24]. First, 1.0 g of flaky graphite (325 mesh) was dissolved into 50 mL CTAB (cetyltrimethylammonium chloride, 0.12 mol/L) solution by ultrasonication for 10 h. Then the solution deposited for 24 h and centrifuged to remove the multi-layer graphene, the supernate was kept at room temperature. Second, 5 mmol (1.2454 g) of $Co(CH_3COO)_2{\cdot}4H_2O$ was added to the as-prepared supernate (about 0.15 g/L) slowly with magnetic stirring for 1 h. An aqueous suspension of urea [$Co(NH_2)_2$] was added to the mixture slowly, stirred for 2 h. Then the solution was transferred to a Teflon line stainless steel autoclave and heated at 433 K for 8 h. After cooling at room temperature, the solution was washed with deionized water and absolute ethanol, and dried at 333 K in a vacuum oven for 24 h. Finally, the powder was transferred to a quartz boat and heated to 773 K for 3 h. At last, the Co_3O_4/graphene powder (CGP) was successfully synthesized.

2.3. Catalyst characterizations

A Bruker-D8 X-ray diffraction (XRD) with Cu Kα radiation ($\lambda = 1.5418$ Å) was used to analyze the sample structure. The morphology and microstructure of sample was examined by a SU-1500 Field Emission Scanning Electron Microscope (FESEM). The change in chemical bonding in the surface and the structure was investigated by Fourier transform infrared spectroscopy which was conducted on a SHIMADZU FTIR-8400S. Raman spectra were monitored by a labRAM HR Evolution Raman spectrometer operating at 514 nm. X-ray photoelectron spectroscopy (XPS) analysis was carried on a ESCALAB 250 photoelectron spectrometer (Thermo VG Scientific, USA) with Al Kα (1486.3 eV) as the X-ray source. The surface area of the samples was observed on a Gemini VII 2390 BET (Micromeritics, USA). Thermogravimetric analysis (TGA) was carried on a Perkin-Elmer Diamond TG/DTA thermal analyzer with a heating rate of 10 K/min.

2.4. Catalyst performance

Here, 100 mL solution of Orange II (0.2 mM) was placed in a glass vessel. A solution of oxone (1 mM) was dissolved in the aqueous solution as the oxidant and a solution of $NaHCO_3$ was used to adjust the pH value to neutral. Then, the catalyst (0.05 g/L) was added to the mixture as the reaction began. The degradation rate was measured using UV–vis spectrophotometry (SHIMADZU UV-2500) at the maximum absorption band (486 nm). To compare the performance of the CGH, pure Co_3O_4, GH and Co_3O_4/graphene powder (CGP) composite, the conditions of the reaction were changed with or without PMS and adjusting pH. To test the stability of the samples, the catalyst was dried in a vacuum oven overnight without any treatment prior to the next recycle.

2.5. Electrochemical measurements

The electrochemical measurements were performed in KOH (0.1 M) solution using CHI 660E Electrochemical Analyzer, which were analyzed in a standard three-electrode cell. A reference electrode and a counter electrode were utilized with an Ag/AgCl and a Pt foil, respectively. The working electrodes were prepared by coating 5 µL of samples suspension (catalyst: 5 mg, ethanol: 495 µL, water: 495 µL, 5 wt. % Nafion: 5 µL) onto a glassy carbon electrode (GCE, 0.07 cm^2). Cyclic voltammetry (CV) measurements were tested at a scan rate of 50 mV/s from −0.4 to 0.6 V *versus* Ag/AgCl.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the synthetic procedure of the CGH catalyst. Firstly, the hydrogel was prepared from the well-mixed solution of the GO and $Co(CH_3COO)_2$ via a thermal process. The GO could then be reduced into graphene sheets by glycol, after which the graphene sheets were shown to be overlapping and coalescing due to the glycol. Co_3O_4 particles-containing 3D structure graphene sheets were decomposed to cobalt acetate. The catalysts were finally obtained by freeze-drying the samples to form a cylinder.

The morphology of the CGH was investigated by scanning electron microscopy (SEM). Fig. 2(a, b) shows that as-prepared GH has a 3D-hierarchically porous structure, with pore sizes in the range of tens of nanometers to a few micrometers [25]. In Fig. 2(c–f), the CGH composite and GH had similar morphological characteristics with a 3D-hierarchically porous structure [26]. This structure increases the specific surface area of the composite, which can provide more active sites. The Co_3O_4 particles (1–2 µm in size) encapsulate inside the graphene sheet and are loaded on graphene uniformly with a chemical bond [27], which may be due to the glycol as the cross linker in the hydrothermal process.

To investigate the compositions and crystalline properties of the catalyst, the XRD patterns of CGH, pure Co_3O_4, GH and GO are shown in Fig. 3. All peaks of Co_3O_4 and CGH correspond to (111), (220), (311), (222), (400), (422), (511), and (440) reflections, respectively; these peaks were also indexed with the characteristic peaks of Co_3O_4 face-centered cubic phase (JCPDS no. 43-1003), indicating the crystalline nature of Co_3O_4. The sharp diffraction peak of GO at 10.6° was typical for GO, indicating the extent of GO oxidation. In comparison, a weak and broad diffraction peak appeared at around 26° [28], implying the formation of graphene in the composite.

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