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Synthesis of α-Fe_2O_3/TiO_2 nanotube arrays for photoelectro-Fenton degradation of phenol

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ABSTRACT

Developing new nanophotocatalysts and identifying their roles are highly attractive in environmental protection and energy utilization. Photoelectro-Fenton process is an environmentally friendly technology and has a wide application in the control of environmental pollutants. However, efficient nanophotocatalysts responsive to visible light are still few. In this work, we have successfully synthesized a uniformly dispersed α-Fe_2O_3/TiO_2 nanotubes hetero-nanostructure by electrochemical deposition method for the degradation of phenol. Compared with the separate α-Fe_2O_3 nanoparticles and TiO_2 nanotubes, the composite α-Fe_2O_3/TiO_2 nanotubes electrodes were more effective in the photoelectro-Fenton degradation of phenol and a 100% removal efficiency of phenol was obtained after 60 min treatment. The composite α-Fe_2O_3/TiO_2 electrodes showed an enhanced absorbance in visible light region and had good stability to photoelectro-Fenton reactions. The role of α-Fe_2O_3 nanoparticles in various Fenton-related processes were systematically investigated. The results indicate that α-Fe_2O_3/TiO_2 nanotubes are promising material for pollution prevention.

1. Introduction

Water treatment using environmentally friendly technologies is an attractive research topic. Advanced oxidation processes (AOPs) have been proven to be effective means for environmental pollutant treatment, especially for biorefractory organic pollutants [1–3]. The photoelectro-Fenton process, one of the AOPs technologies, has attracted considerable attention due to its high efficiency [4–6]. During photoelectrocatalysis, titanium dioxide (TiO_2) is frequently used as the photocatalyst since it is nontoxic and environmentally friendly [7]. TiO_2 has three common crystalline phases, including anatase, rutile, and brookite. Photocatalytic research mainly focuses on anatase and rutile. Studies generally indicate that the metastable anatase tends to show higher photocatalytic activity compared to the stable rutile [8,9]. TiO_2 nanoparticles (NPs) have been used for the degradation of an azo dye, which indicates 98.8% mineralization of 20 mg/L dye at 6 h [10]. In addition, novel TiO_2 NPs were successfully synthesized to induce the adsorption of ethylene pollutant [11].

However, the large band gap of TiO_2 limits its photoresponse to the ultraviolet (UV) region. As we all know, only a small proportion (4%) of the solar spectrum falls in the UV region [12]. To overcome this disadvantage and make full use of solar energy, much research has been carried out to sensitize TiO_2 so that it is possible to utilize the visible region of the solar light [13–15]. Another promising method is to modify TiO_2 with other narrow band gap materials that are able to absorb the photons in the visible range [16,17]. Fe_2O_3 is a promising candidate since it has the advantages of low band gap (2.2 eV), low cost, and nontoxicity [18,19]. α-Fe_2O_3 is the most stable form of iron oxide [20]. It can absorb and make use of visible light. Some researchers have reported that TiO_2 modified by Fe_2O_3 showed higher photo-activity than those of unmodified TiO_2 [21,22]. Kontos et al. dipped TiO_2 nanotubes (NTs) in iron oxide aqueous suspensions of variable concentrations to functionalize the TiO_2 NTs for the degradation of methyl orange azo-dyes. The methyl orange decomposition rate using TiO_2 NTs functionalized by iron oxide NPs showed an increase at 5 mg/mL iron oxide concentration compared to the bare TiO_2 NTs. However, the promotion was very little and the decrease in the photocatalytic activity was observed at high load of iron oxide NPs. TiO_2 NTs openings were partially blocked by a dense layer of iron oxide aggregates [23]. The negative effect of Fe_2O_3 modification on TiO_2 was also reported. Jeon et al. found that Fe_2O_3/TiO_2 has ca. 40%-reduced photoelectrochemical (PEC) activity as compared to TiO_2 NPs under AM 1.5 light. The decreased PEC behaviors of Fe_2O_3/TiO_2 were attributed to the hematite-induced charge recombination due to an energy level mismatch between TiO_2 and hematite [24]. Thus, there are the inconsistent findings reported on the performance of TiO_2 modified by Fe_2O_3. The preparation process and the interface architecture probably play an important role in increasing or decreasing the PEC activity of Fe_2O_3/TiO_2 composite electrodes. New synthetic methods are required to improve the PEC activity of Fe_2O_3/TiO_2

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composite electrodes and more work needs to be done to identify the role of Fe_2O_3.

In this paper, a uniformly dispersed α-Fe_2O_3 NPs/TiO_2 NTs hetero-nanostructure was developed by a new electrochemical deposition method for the degradation of environmental pollutants. Phenol was chosen as the model pollutant. Dipping method was also used to prepare the α-Fe_2O_3 NPs/TiO_2 NTs composited electrodes for the comparison. The removal efficiency of phenol using the α-Fe_2O_3 NPs/TiO_2 NTs synthesized by electrochemical deposition method was significantly improved relative to those prepared by dipping method. Field emission scanning electron microscope images showed that the TiO_2 NTs openings were not blocked by Fe_2O_3 aggregates. Various Fenton-related processes, such as electro-Fenton, visible light photoelectro-Fenton, and UV–visible light photoelectro-Fenton, were investigated to evaluate the degradation performance of the electrodes. To explore the role of α-Fe_2O_3 NPs, both the Dispersed system and Fixed system were studied. In the Dispersed system, Fe_2O_3 NPs were dispersed in the electrochemical cell, and TiO_2 NTs were used as anodes. In the Fixed system, Fe_2O_3 NPs were fixed on the surface of TiO_2 NTs, and the composite Fe_2O_3/TiO_2 NTs were used as anodes. Depending on the changes of the model pollutants and the intermediates, the role of α-Fe_2O_3 NPs and a possible reaction mechanism were suggested.

2. Experimental methods

2.1. Preparation of TiO_2 nanotubes

TiO_2 NTs were fabricated on a Ti foil by the electrochemical anodization method. Ti foil (20 mm × 25 mm) was polished with sandpaper, and then ultrasonically cleaned with acetone, ethanol, and distilled water, in turn. A two-electrode borosilicate glass cell was used to perform the anodization process. The pretreated Ti foil was used as an anode and Pt sheet as the cathode. A mixed solution of 0.5 wt% sodium fluoride (NaF) and 0.5 M anhydrous sodium sulfate (Na_2SO_4) was prepared as the anodization electrolyte. All reagents used in this study were reagent grade. All the experiments were carried out at 20 V for 5 h with constant magnetic stirring. The anodized samples were washed with distilled water and dried in air. The as-formed TiO_2 NTs were annealed in a muffle furnace at 500 °C for 2 h to convert the amorphous TiO_2 to crystalline form.

2.2. Preparation of α-Fe_2O_3 nanoparticles

α-Fe_2O_3 NPs were prepared using ferric trichloride ($FeCl_3$) as a precursor. An aqueous solution (0.05 M, 100 mL) was prepared by mixing $FeCl_3$ and distilled water. The pH value of aqueous solution was adjusted to 2 and the solution temperature was controlled at 20 °C. During the experiment, Fe foil (Mountain Technical, 99.95% purity) were used as the anode and cathode. The current density was 0.2 A/cm^2. When the electrodeposition began, black iron NPs were generated on the cathode and some suspended in the solution. The resulting NPs were loosely attached to the electrode surface and could be easily separated from the cathode. The detached NPs were washed with distilled water three times, dried at 60 °C and annealed at 600 °C for 10 min to obtain α-Fe_2O_3 NPs.

2.3. Synthesis of α-Fe_2O_3/TiO_2 nanotubes electrodes using the dipping method

To explore the role of α-Fe_2O_3 NPs, we dipped the TiO_2 NTs in the aqueous suspensions of α-Fe_2O_3 NPs with a concentration of 5 mg/mL [23]. Before the dipping process, α-Fe_2O_3 were completely dispersed using ultrasound sonication. After being dipped, the α-Fe_2O_3/TiO_2 NTs electrodes were thoroughly washed with distilled water and dried at room temperature.

2.4. Synthesis of α-Fe_2O_3/TiO_2 nanotubes electrodes using the electrochemical deposition method

To optimize the α-Fe_2O_3/TiO_2 NTs electrodes, the electrochemical deposition method was adopted to synthesize the α-Fe_2O_3/TiO_2 NTs. A two-electrode system was used with TiO_2 NTs electrodes as the cathode and Pt sheet as the anode. First, the TiO_2 NTs electrodes were soaked in a 0.05 M ferric nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) aqueous solution for 10 min, always subjected to ultrasound sonication before soaking. Then the TiO_2 NTs electrodes were transferred into a new medium that only contained an inert supporting electrolyte (0.1 M Na_2SO_4). The potentiostatic DC electrodeposition was carried out with a constant potential of 8 V for 20 min and the temperature of the electrolyte was maintained at 85 °C. After the electrodeposition in this medium, Fe NPs were deposited into the interior tubes of TiO_2 electrode while minimizing deposition at the tube entrances (Fe/TiO_2-NTs). A desired deposition amount of Fe in the nanotubes was obtained after several repetitions. Then the Fe/TiO_2-NTs electrodes were connected as the anode and Pt sheet was the cathode. The material was electrochemically oxidized with a potential of 8 V for 2 min at room temperature using another alkaline electrolytic bath prepared by dissolving 1 M KOH in distilled water. After this electrochemical oxidization, Fe/TiO_2-NTs were converted into the corresponding oxides Fe_2O_3/TiO_2-NTs. The resulting Fe_2O_3/TiO_2-NTs samples were rinsed with distilled water and dried at a low temperature.

2.5. Characterization

A field emission scanning electron microscope (FE-SEM; Hitachi S-4700 II) was used to characterize and analyze the structure of the prepared samples, including TiO_2 NTs, α-Fe_2O_3 NPs and the composite α-Fe_2O_3/TiO_2 NTs electrodes. The micrographs were taken in an operating accelerating voltage of 15.0 kV. The crystal properties were analyzed by X-ray diffraction (XRD) using a diffractometer with Cu Kα radiation (Netherlands PNAlytical X'Pert PRO). The accelerating voltage and applied current were 40 kV and 40 mA, respectively. Light absorption properties were measured using UV–vis diffuse reflectance spectra (Shimadzu, UV–3150) with a wavelength range of 220–600 nm. The concentration of iron ions in solution after photoelectro-Fenton reaction was analyzed using an atomic absorption spectrometer (Thermo iCE 3300 × GFS).

2.6. Heterogeneous photoelectro-Fenton degradation of pollutants

The performance of composite Fe_2O_3/TiO_2-NTs electrodes for photoelectro-Fenton degradation was evaluated using phenol as a model pollutant. All the experiments were carried out in a glass reactor with constant magnetic stirring, using 0.2 M Na_2SO_4 as the electrolyte. The initial concentration of the phenol aqueous solution was 10 mg/L during the experiment. The pH value of initial solution was adjusted to 3 with H_2SO_4 or NaOH solution. To further investigate the role of α-Fe_2O_3 NPs, three different systems were used for the degradation of phenol:

Dispersed system: α-Fe_2O_3 NPs (2 mg) were added into 10 mg/L phenol aqueous solution (100 mL) in each experiment. A nickel electrode and TiO_2 NTs electrodes were used as the cathode and anode, respectively. The applied voltage was 5 V, which was provided by DC Constant Current Power. After the first specimen (about 2 mL) was taken, 1 mL of the H_2O_2 solution (3%) was added into the suspension, and then the degradation was initialized. The Fenton