



Photo-Fenton degradation of ammonia via a manganese–iron double-active component catalyst of graphene–manganese ferrite under visible light

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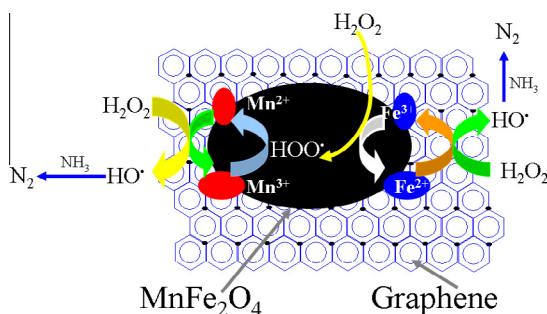
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HIGHLIGHTS

- Graphene–manganese ferrite is a double-active component photo-Fenton catalyst.
- Both manganese and iron promote simultaneously the degradation of ammonia.
- Ammonia is degraded into dinitrogen gas, showing the thorough removal of ammonia.
- Graphene–manganese ferrite is recoverable and reusable.

GRAPHICAL ABSTRACT

A double-active component photo-Fenton catalytic system for the degradation of ammonia.



ARTICLE INFO

Article history:

Received 15 February 2015
Received in revised form 11 July 2015
Accepted 15 July 2015
Available online 29 July 2015

Keywords:

Graphene–manganese ferrite
Double-effect catalyst
Photo-Fenton
Ammonia
Degradation

ABSTRACT

Graphene–manganese ferrite (rG–MnFe₂O₄) was developed to degrade NH₃. It was characterized by X-ray diffraction, transmission electron microscopy, Fourier-transform infrared spectroscopy, and X-ray photoelectron spectroscopy (XPS). The results using rG–MnFe₂O₄ as a heterogeneous photo-Fenton catalyst showed a degradation of 92.0% was achieved through visible light irradiation of 50.0 mg L⁻¹ NH₃-N solution at pH 10.5 in the presence of 1.0 mmol/L H₂O₂ for 10 h. The product for the degradation of NH₃ was identified as N₂ but not NO₂⁻ or NO₃⁻. The degradation of ammonia follows the pseudo first order reaction law, the average apparent reaction rate constant is obtained to be 0.0396 min⁻¹ under white light irradiation. XPS measurements showed that Mn(III) and Fe(II) are formed during photo-Fenton degradation of NH₃, which suggests that Mn and Fe simultaneously participate in the photocatalytic cycle. Thus, rG–MnFe₂O₄ is a double-effect photo-Fenton catalyst. The double-active catalytic mechanism was explored.

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1. Introduction

Ammonia (NH₃/NH₄⁺) has recently become a major aquatic contaminant. NH₃, as a recalcitrant water contaminant, is the final

nitrogen species contaminant in landfill leachates released by bio-fermentation [1–3] and the predominant product mineralized during photocatalytic degradation of nitrogen-containing organic pollutants [4–7]. That is, NH₃ is the most stable form of nitrogen-containing species, and breakage of the N–H bond is very difficult to achieve.

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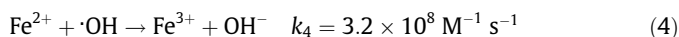
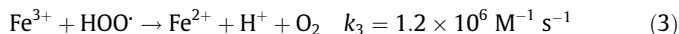
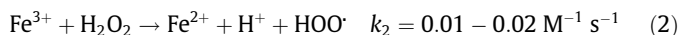
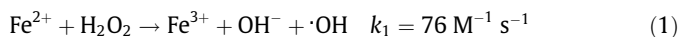
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NH₃ removal can be realized via nitrification in the presence of nitrobacteria, during which NH₃ is first converted into nitrite and/or nitrate and then thoroughly denitrified in the presence of denitrobacteria. During denitrification, nitrite or nitrate is reduced to nitrogen gas [8–11]. These steps considerably increase costs associated with NH₃ removal from the environment.

TiO₂ has been used to break N–H bonds and explore the mechanism of NH₃ decomposition [12,13]. Some researchers have shown that the photocatalytic technique can destroy N–H bonds completely [14–20]. However, most photocatalysts developed for this purpose are mainly TiO₂-based, few other photocatalysts have been explored to degrade NH₃. However, the TiO₂-based material can make use of only approximately 4% of the available solar energy due to wide band gap and 43% of the visible light energy cannot be utilized effectively. As such, novel photocatalysts that respond to visible light irradiation must be developed to decompose NH₃.

Manganese ferrite (MnFe₂O₄) is a magnetic material that can be easily separated from reaction media by an external magnetic field. MnFe₂O₄ presents multiple absorbance bands located at 430, 576, and 745 nm, which are attributed to the possible *d–d* transitions involving Mn^{3+/2+} or Fe³⁺ ions and ligand-to-metal charge-transfer transition at 295 nm [21]. Thus, it is a potential wide-spectrum catalyst that can respond to the solar spectrum range from ultraviolet light to visible irradiation. Unfortunately, since MnFe₂O₄ alone is photocatalytically inactive under visible light irradiation [5], combination of this material with a photosensitizer such as graphene is necessary to transform it into an appropriate photocatalyst [21,22]. In fact, graphene can increase photocatalytic activities and widen spectral responses to solar irradiation [23–28]. rG–MnFe₂O₄ hybrid materials have not been previously studied as double-effect heterogeneous photo-Fenton catalysts for degradation of recalcitrant NH₃. In the current study, we prepare a rG–MnFe₂O₄ hybrid catalyst and evaluate its photo-Fenton catalytic activities during NH₃ decomposition under visible light irradiation in the presence of hydrogen peroxide (H₂O₂).

Fe(II,III) ions are known to function effectively as heterogeneous photocatalytic components. The transition from Fe(II) to Fe(III) generates highly active hydroxyl (·OH) radicals in the presence of H₂O₂. The following chemical reactions are involved [29–31]:



As-generated highly active hydroxyl radicals can degrade organic pollutants. Similarly, Mn(II,III) in the MnFe₂O₄ system, is like Fe(II,III) in the graphene oxide (GO)–NiFe₂O₄ system [30], can transform each other in alkaline solution [32]. Mn and Fe ions are believed to present heterogeneous catalytic functions in the MnFe₂O₄ system. Therefore, we attempted to design and synthesize a heterogeneous rG–MnFe₂O₄ photocatalyst that can degrade NH₃ in the presence of H₂O₂ under visible irradiation. As our previous report on a GO–NiFe₂O₄ photocatalyst [30], we expect that the rG–MnFe₂O₄ catalyst developed in this work can effectively degrade recalcitrant NH₃ via a double-effect heterogeneous photo-Fenton reaction.

2. Experimental

2.1. Chemicals

Graphite powder (average particle size, 30 μm) was purchased from Shanghai Colloid Chemical Plant (Shanghai, China). Ferric chloride hexahydrate (FeCl₃·6H₂O) and sodium hydroxide (NaOH) were purchased from Tianjin Damao Chemical Factory, China. Manganese dichloride tetrahydrate (MnCl₂·4H₂O), ammonium sulfate ((NH₄)₂SO₄), and ammonium chloride (NH₄Cl) were obtained from Nanjing Chemical Reagent Co., Ltd. All reagents used were of analytical grade and applied without further purification. All solutions were prepared with 18.2 MΩ cm deionized Milli-Q water.

2.2. Synthesis of rG–MnFe₂O₄

MnCl₂·4H₂O (1.9790 g, 0.01 mol) and FeCl₃·6H₂O (5.4058 g, 0.02 mol) were separately dissolved in 15.0 mL of deionized water. The solutions were then stirred together to form Solution A. MnCl₂ solution appeared pink, and FeCl₃ solution was yellow. pHs of both solutions were about 6.5–7.0. The mixture of MnCl₂ and FeCl₃ solution appeared out in grayish yellow turbidity. The final pH was about 11–12 after the addition of NaOH. GO was synthesized via a modified Hummers method as previously described [30]. The as-synthesized GO (92.2 mg, 4% of the MnFe₂O₄ mass) was dispersed in 10.0 mL of deionized water by an ultrasonic vibrator, and the resultant solution was denoted as solution B. Solution A was added dropwise to Solution B under stirring. NaOH (3.2 g, 0.08 mol) was dissolved in 10.0 mL of deionized water, and this solution was added dropwise to the mixed suspension solution described above under continuous stirring. Deionized water was also added to the suspension to obtain a final volume of 60 mL. The suspension solution was then transferred to a 100 mL Teflon-lined stainless-steel autoclave that was subsequently sealed and maintained at 180 °C for 10 h. The solution was cooled to room temperature and filtered to obtain rG–MnFe₂O₄ precipitates. The products were rinsed thrice with water to remove excess NaOH and other electrolytes, and the magnetic powder was obtained after sintering at 200 °C for 4 h. This magnetic powder was used for the characterization and photocatalytic tests. Pure MnFe₂O₄ was similarly prepared for comparison.

2.3. Structural characterization of rG–MnFe₂O₄

X-ray diffraction (XRD) was performed with an X'Pert-Pro MPD X-ray diffractometer (Panalytical, Netherlands). The X-ray source emitted Cu-Kα radiation with a wavelength of 0.154 nm at a tube voltage of 40 kV and a tube current of 40 mA. Morphological observations were conducted with a transmission electron microscope (TEM; Tecnai G220; FEI, USA). The rG–MnFe₂O₄ and GO powders were dispersed in water by an ultrasonication device, placed on carbon-coated copper grids, and dried under ambient conditions prior to TEM. A Fourier transform infrared (FT-IR) spectrophotometer (Spectrum BX; PerkinElmer Ltd., USA) was used to characterize group vibrations at an optical resolution of 4 cm⁻¹. The mulls of rG–MnFe₂O₄ were supported by a KBr plate.

X-ray photoelectron spectrometry (XPS) with an XSAM 800 apparatus was used to characterize the valence states of Fe and Mn in the rG–MnFe₂O₄ samples before and after irradiation to elucidate the relevant reaction mechanism. The binding energy (*E*_b) scale was calibrated with respect to the carbon 1s peak at 284.60 eV. The aluminum K_α 1.2 line (*hν* 1486.60 eV) was used as the X-ray excitation source, and each powder sample was dispersed on a gold-plated copper surface. Spectra were recorded

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