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$NiFe_2O_4$/g-C_3N_4 heterojunction composite with enhanced visible-light photocatalytic activity

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Abstract Spinel structure nickel ferrite ($NiFe_2O_4$) doped graphitic carbon nitride (g-C_3N_4) photocatalyst $NiFe_2O_4$/g-C_3N_4 was synthesized by the coprecipitation route to enhance the photocatalytic activity for the visible-light driven degradation of methyl orange. The $NiFe_2O_4$ doping content is responsible for the microstructure and photocatalytic activity of $NiFe_2O_4$/g-C_3N_4 samples. Compared with pure $NiFe_2O_4$ and g-C_3N_4, the 2-$NiFe_2O_4$/g-C_3N_4 composite with $NiFe_2O_4$ doping of 2.0 wt% exhibited excellent photocatalytic activity and superior stability after five runs for degrading methyl orange under visible light irradiation. The catalytic activity of 2-$NiFe_2O_4$/g-C_3N_4 sample produced using the coprecipitation route was higher than those of conventional 2-$NiFe_2O_4$/g-C_3N_4 bulks prepared by the impregnation approach. The prepared samples for the photocatalytic degradation of methyl orange followed pseudo-first-order reaction kinetics. It's ascribed to the synergistic effect between $NiFe_2O_4$ and g-C_3N_4, which can inhibit the recombination of photoexcited electron-hole pairs, accelerate photoproduced charges separation, and enhance the visible light absorption.

1. Introduction

Photocatalysis technology, as a green sustainable avenue to convert solar energy into chemical energy and energy fuels, has been widely paid attention to address the environmental remediation and solar energy conversion [1–3]. The semiconductor catalysts, such as TiO_2, Fe_2O_3, ZnO, and CdS, are intensively performed for the production hydrogen from splitting water, degradation of organic pollutants, synthesis of hydrocarbon compounds, and methanation of carbon oxide [4–11]. However, these catalysts are not suitable for the effective utilization of solar energy under visible light irradiation due to large band gap energy, fast recombination of electron-hole pairs, and low surface area [12–14]. It is thus urgent to develop novel semiconductor catalysts with effective photocatalysis in visible-light applications.

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Graphitic carbon nitride (g-C_3N_4), a metal-free polymeric semiconductor with the band gap of 2.7–2.8 eV, is one of the most potential visible-light catalysts due to its high condensation and tri-s-triazine ring structure [15–17]. Nevertheless, g-C_3N_4 is greatly deactivated by low electrical conductivity, high recombination of charge carriers, and deficient absorption of solar energy above 460 nm [18–22]. Several strategies such as doping modification, electronic structure modulation, and constructing g-C_3N_4-based composites are attempted to broaden visible-light absorption and strengthen photocatalytic activity of g-C_3N_4 materials [23–26]. The doping of inorganic particles into g-C_3N_4 matrix is an effective approach to modify the energy band configuration and electronic structure [27–30]. The effective anchoring of inorganic or organic materials on the g-C_3N_4 surface favors the optimized visible-light photoactivity. Combination between g-C_3N_4 and semiconductor such as Ag_3VO_4, CdS, ZnO, Ag_2WO_4, NiS, and WO_3 can enhance photocatalytic activity under visible-light irradiation because of the cooperative effect of heterojunction structure with interfacial charge-transfer effects and effective light harvesting [31–36]. In recent years, spinel structure ferrite (MFe_2O_4, M = Zn, Ni, and Co) based samples have aroused great interest for water splitting into hydrogen and degradation of organic pollutants [37–45]. Compared with pure $NiFe_2O_4$ with inferior photocatalytic activity even though in the Fenton reaction, the matching energy level of g-C_3N_4 and $NiFe_2O_4$ is contributed to the separation and immigration of electron-hole pairs [37,38]. The g-C_3N_4-based heterojunction photocatalysts doped with MFe_2O_4 can also accelerate the electron-hole separation, inducing to the fascinating optical property. However, the detailed fundamental study of spinel structure $NiFe_2O_4$ doped g-C_3N_4 ($NiFe_2O_4$/g-C_3N_4) for the visible-light driven degradation of methyl orange is scarce in previous works.

This work focused on the fabrication of g-C_3N_4-based heterojunction material combined with spinel $NiFe_2O_4$ ($NiFe_2O_4$/g-C_3N_4) via a coprecipitation route (NiFe/CN), and performed for the photocatalytic degradation of methyl orange under visible light irradiation. Compared with pure $NiFe_2O_4$ and g-C_3N_4, $NiFe_2O_4$/g-C_3N_4 sample with optimized $NiFe_2O_4$ doping (2-NiFe/CN) presented excellent visible-light photocatalytic activity and slight deterioration for the degradation of methyl orange. The 2-NiFe/CN bulks exhibited higher photodegradation efficiency than that of 2-NiFe/CN-*D* generated by impregnation method.

2. Experimental

2.1. Preparation of catalysts

$NiFe_2O_4$/g-C_3N_4 composites (NiFe/CN) with $NiFe_2O_4$ doping content of 1–5 wt% were synthesized using a coprecipitation approach. All chemicals were used without further purification. In a typical process, melamine ($C_3H_6N_6$) and ammonia ($NH_3{\cdot}H_2O$) were added into 200 mL dimethyl sulfoxide (C_2H_6OS) to form solution A. Cyanuric acid ($C_3H_3N_3O_3$), nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), and ferric nitrate ($Fe(NO_3)_3{\cdot}6H_2O$) in stoichiometric proportion were dissolved into 200 mL dimethyl sulfoxide (C_2H_6OS) solution to form solution B. The solution B was slowly added to solution A under vigorous stirring at room temperature. The above mixture solution was then centrifuged, washed with ethanol and distilled water four times, dried at 353 K for 12 h, and calcined at 823 K for 3 h to obtain NiFe/CN sample. According to above route, NiFe/CN samples doped with $NiFe_2O_4$ content of 1–5 wt% were generated and labeled as 1-NiFe/CN, 2-NiFe/CN, 3-NiFe/CN, 4-NiFe/CN, and 5-NiFe/CN. The g-C_3N_4 produced via the coprecipitation approach and the thermal polymerization route was denoted as g-C_3N_4 and g-C_3N_4-*D*, respectively. g-C_3N_4-*D* bulks were prepared by a traditional thermal polymerization route, of which 10 g of urea was placed in an alumina crucible and annealed at 823 K for 3 h to collect yellow product [46–48]. $NiFe_2O_4$/g-C_3N_4-*D* (NiFe/CN-*D*) sample was generated by the impregnation route. Typically, 1 g of g-C_3N_4-*D* bulks was added to 100 mL aqueous solutions including different amounts of $Ni(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}6H_2O$ in stoichiometric proportion. The above solution was continually stirred at room temperature for 4 h, stirred at 353 K to evaporate excessive water, dried at 373 K for 12 h, and calcined at 823 K for 3 h.

2.2. Characterization of catalysts

XRD patterns of the fabricated samples were taken on a Bruker D8 Advance X-ray Powder Diffractometer equipped with a Cu Kα radiation (λ = 0.15406 nm). Fourier transforms infrared spectra (FT-IR) were obtained on Bruker VECTORTM 22 FTIR spectrometer with the region of 400–4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) patterns were collected by a Kratos Axis UltraDLD equipped with a hemispherical electron energy analyzer. The $NiFe_2O_4$ doping mass was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) method on Varian 710-ES equipped with a 1.12 megapixel CCD detector. N_2 sorption isotherms were achieved using a Quantachrome autosorb automated gas sorption analyzer (NOVA 2200e). Scanning electron microscopy (SEM) images were recorded with a JSM-5610LV/INCA microscope. Transmission electron microscopy (TEM) images were obtained by a Philips Tecnai G220 operated at 200 kV. The high resolution transmission electron microscopy (HRTEM) images were detected on JEM-2100 operated at 200 kV. UV–visible diffuse reflectance spectra (UV–vis DRS) was recorded on Shimadzu UV-2101 PC spectrophotometer with an ISR-240A integrating sphere attachment. The photoluminescence (PL) spectra were observed on Varian Cary Eclipse spectrometer. The electron spin resonance (ESR) signals of radicals were obtained on a Bruker model ESR JES-FA200 spectrometer.

2.3. Evaluation of catalysts

The $NiFe_2O_4$/g-C_3N_4 samples were performed for the photodegradation of methyl orange under visible light region generated from a 300 W Xe lamp with a 420 nm cutoff filter. In a typical process, 0.2 g sample was added to the methyl orange solution (200 mL, 10 mg L^{-1}) and magnetically stirred in dark for 2 h to achieve absorption–desorption equilibrium before reaction. At regular time intervals, 10 mL above solution was sampled and centrifuged to remove the solid particles. The concentration of methyl orange was evaluated by a Hitachi U-3010 UV–vis spectrophotometer. The photocatalytic stability of $NiFe_2O_4$/g-C_3N_4 samples was performed for five cycles. The first cycle of experiment was carried out for 60 min under

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