Journal of Photochemistry & Photobiology A: Chemistry 360 (2018) 132–136

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Full Length Article

Dye-sensitized hematite compososite photocatalyst and its photocatalytic performance of aerobic annulation

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ARTICLE INFO

Keywords:
Photocatalyst
Hematite
Chemical synthesis

ABSTRACT

A visible light initiated catalyst (DP-pfa@Fe_2O_3) is synthesized and used as a photocatalyst for the synthesis of pyrazoles under mild reaction conditions. Holes (h^+) and · OH are the essential for the light-induced the pyrazole annulation reaction using water as oxygen source. Results demonstrate that photocatalyzed reaction of methyl hydrazine and 2-benzylidenemalononitrile produced 2-((2-methylhydrazinyl)(phenyl)methylene)malononitile, which can transfer into pyrazoles in the presence of · OH. Our results provide a new catalyst and an economic synthetic method for the synthesis of pyrazoles through aerobic annulation.

1. Introduction

Photocatalysis, which is an environmental-friendly technology to convert solar energy into chemical energy, has been attracting much research interest [1]. There are many materials which show high photocatalytic activity irradiated with light [2]. Hematite (α-Fe_2O_3) is one of the promising photocatalysts due to its high chemical stability, high efficiency and low-cost [3]. It has been reported that increasing the absorption of light and decreasing the recombination rate of the photogenerated charge carriers can enhance the photocatalytic activity [4]. Researchers have tried to use many methods to improve photocatalytic properties of hematite, such as doping with other materials, modification of surface structure, formation of composites and heterostructures, etc [5]. Among of these methods, dye-sensitization is an innovative method to improve photo-responsibility of photocatalyst. Some dyes have been studied with semiconductor for the degradation of pollutants, for example, porphyrin, rhodamine and methylene blue [6].

On the other hand, photocatalytic organic reactions especial photoredox reactions have emerged as a "green" tool for chemical transformation [7]. Studies show that photocatalyst can lower the reaction temperature, reduce side reactions and speed up chemical reaction by promoting to generate reactive intermediates [8]. Current photoredox reactions research is mainly focused on the oxidation of alcohols and amines, C—H activation reaction and classic cross-coupling reactions, so on [9]. In our previous work, $Ru^{II}(bpy)_3Cl_2{\cdot}6H_2O$ has been successfully used to photocatalyze aerobic annulation [10]. Considering the high cost of $Ru^{II}(bpy)_3Cl_2{\cdot}6H_2O$, we design and synthesis a novel dye-sensitized hematite composite (DP-pfa@Fe_2O_3) as a photocatalyst of aerobic annulation. In this paper, 10-(4-((3,4-dihydroquinolin-1(2H)-yl)methyl)phenyl)-5,5-difluoro-1,3,7,9-tetra- methyl-5H-44λ^4,5λ^4-dipyrrolo[1,2-*c*-2′1′f][1,3,2]diazaborinine (DP) is used as a sensitizer to absorb visible light due to its excellent photophysical properties, such as long-wavelength absorption, high quantum yields, photochemical stabilities and fluorescence emission in the visible region [11]. After being sensitized by DP, the absorption intensity of hematite is greatly improved. The photocatalytic results demonstrate that DP-pfa@Fe_2O_3 is a promising visible-light-driven photocatalyst for the synthesis of pyrazoles by aerobic annulation, which will provide a mild synthetic method of pyrazoles.

2. Experimental

2.1. Materials

All chemicals were analytical grade and used as received without further purification. Pyrrole-2-carboxylic acid, polyvinylpyrrolidone (PVP k30), 2,4-dimethylpyrrole, *p*-chloromethylbenzoyl chloride, 1,2,3,4-tetrahydroisoquinoline, triethylamine, boron trifluoride ether, cyanide, benzaldehyde and methyl hydrazine (40% aqueous solution) were purchased from Aladdin Reagent Co. Ltd., Shanghai. Ferric chloride hexahydrate ($FeCl_3.6H_2O$), sodium hydroxide (NaOH) and concentrated hydrochloric acid (HCl) were supplied by Sinopharm Chemical Reagent Co. Ltd, China. Deionized water was obtained from a Millipore Milli-Q system.

2.2. Characterization

X-ray powder diffraction (XRD) measurements of samples were

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https://doi.org/10.1016/j.jphotochem.2018.04.037
Received 19 February 2018; Received in revised form 13 April 2018; Accepted 18 April 2018
Available online 22 April 2018
1010-6030/

performed on a Bruker D8 diffractometer operated at 40 kV and 40 mA using Cu-Ka radiation (l = 1.54056 A). Infrared spectrawere recorded on a Nicolet-470 spectrophotometer in the

wavenumber range of 4000–400 cm^{-1} using KBr pellets. Electronic absorption spectra were recorded in the 900–190 nm a Varian CARY 50-BIO UV–VIS spectrophotometer. Fluorescence measurements were performed on a fluorescence spectrofluorometer Model CARY Eclipse (VARIAN, USA), a 1.0 cm quartz cell (ex = 325 nm, slit width = 10 nm). TEM was performed at roomtemperature on a JEOL JEM-200CX transmission electron microscope using an accelerating voltage of 200 kV. The EPR spectra of complexes in CH_3CN were acquired at 298 K with a 0.201 mW power, 0.5 G modulation amplitude, and 100 kHz modulation frequency. The volume of O_2 was measured by direct methods, via connecting of the reaction vessel with a U-tube to a calibrated microburet with collection of the gas released. Column chromatography was generally performed on silica gel (200–300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^1H (400 MHz) and ^{13}C NMR (100 MHz) data were recorded on Bruker AVANCE II 400 MHz spectrometer using $CDCl_3$ as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^1H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference.

2.3. Synthesis of pfa@Fe_2O_3

Black pfa@Fe_2O_3 is prepared by adding $FeCl_3.6H_2O$ (0.25 M 20 mL) and PVP (100 mg) into the aqueous of pyrrole-2-carboxylic acid (0.5 M 20 mL). After stirring about 15 min, the mixture is heated at 160 °C for 6 h in a 50 mL autoclave. The products are obtained by filtration, washed three times with ethanol and dried in vacuum.

2.4. Synthesis of 10-(4-((3,4-dihydroquinolin-1(2H)-yl)methyl)phenyl)-5,5- difluoro-1,3,7,9-tetramethyl-5H-44λ^4,5λ^4-dipyrrolo[1,2-c-2′1′-f][1,3,2]diazaborinine (DP)

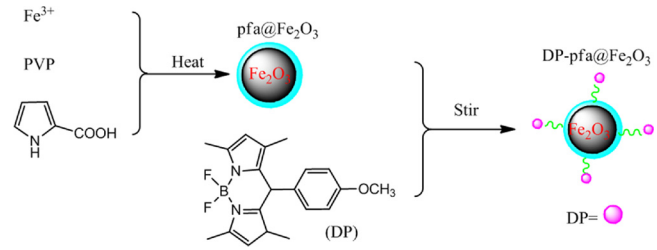
DP is synthesized according to the reported method [12]. Typically, 8-(4-Chlorobenzyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (137 mg, 0.37 mmol) and 3,4-dihydro-2H-1λ-quinoline (72.8 mg, 0.550 mmol) were dissolved in 100 mL acetonitrile, followed by addition of triethylamine (74 mg, 0.74 mmol). The resulting mixture was stirred for 24 h at room temperature. Next, the solution was concentrated and the residues were redissolved in DCM and washed with water. The organic phase was dried over anhydrous Na $_2SO_4$. The residue was purified using silica gel column chromatography (petroleum ether–ethyl acetate (3: 1) to afford green oil (160 mg, 92%). (Found: C,74.52; H,6.31; N, 8.90. Calcd for $C_{29}H_{30}$ BF_2N_5: C, 74.21; H, 6.44; N, 8.95%.); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.55–7.53 (d, *J* = 8 Hz, 2H), 7.26–7.25 (d, *J* = 4 Hz, 2H), 7.14 (m, 3H), 6.98–6.96 (d, *J* = 8 Hz,1H), 5.99 (s, 2H), 3.80 (s, 2H), 3.65 (s, 2H), 2.96–2.93 (t, *J* = 6 Hz, 2H), 2.82–2.79 (t, *J* = 6 Hz, 2H), 2.56 (s, 6H), 1.41 (s, 6H). MS (ESI) Calcd for $C_{29}H_{30}$ BF_2N_5: ([M + H$^+$]) = 470.36, found: *m/z* = 470.54, (100%). UV–vis(CH_2Cl_2/nm) (ε × 10^4, dm^3 mol^{-1} cm^{-1}): 230 (3.15), 337 (0.8), 501 (8.3).

2.5. Synthesis of DP-pfa@Fe_2O_3

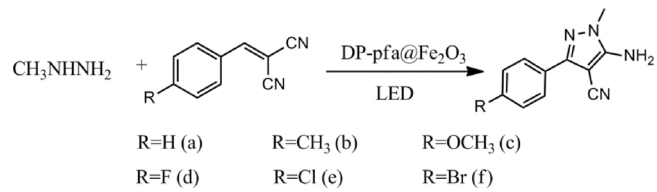
Pfa@Fe_2O_3 (30 mg) and DP (2.5 mg) were suspended in dichloromethane (5 mL), the suspension is stirring for 4 h at room temperature. After centrifugal separation, the products are washed with dichloromethane for several times and dried in vacuum (Scheme 1).

2.6. Photocatalytic annulation reaction

In photocatalytic reactor, DP-pfa@Fe_2O_3 (10 mg), 0.6 mmol of



Scheme 1. Preparation of DP-pfa@Fe_2O_3.



Scheme 2. Photocatalytic reaction of CH_3NHNH_2 and 2-benzylidenemalononitrile derivatives.

methyl hydrazine aqueous solution, 0.5 mmol of 2-benzylidenemalononitrile or its derivatives were added to 4 mL of CH_3CN/H_2O mixture (1:1, v/v). After purging with N_2 for about 10 min, the mixture was illuminated by the LED lamp (450–550 nm, 4W) for 4 h. Then the catalyst was collected by filtration and the product was isolated by silica chromatography after extraction and dryness (Scheme 2).

5-amino-1-methyl-3-phenyl-1H-pyrazole-4-carbonitrile (a). ^1H NMR (400 MHz, $CDCl_3$) & 7.90–7.88 (m, 2H), 7.44–7.39 (m, 3H), 4.54 (s, 2H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) & 150.36, 150.21, 131.11, 129.02, 128.83, 126.23, 115.80, 73.23, 34.76.

5-amino-1-methyl-3-(*p*-tolyl)-1H-pyrazole-4-carbonitrile (b). ^1H NMR (400 MHz, $CDCl_3$) & 7.79 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8 Hz, 2H), 4.34 (s, 2H), 3.70 (s, 3H), 2.40(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) & 151.77, 150.47, 139.04, 129.44, 128.47, 126.11, 115.89, 77.14, 34.70, 21.36.

5-amino-3-(4-methoxyphenyl)-1-methyl-1H-pyrazole-4-carbonitrile (c). ^1H NMR (400 MHz, $(CD_3)_2SO$) & 7.72 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.63 (s, 2H), 3.79 (s, 3H), 3.57 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) & 160.00, 153.56, 149.01, 127.42, 124.73, 116.70, 114.59, 70.05, 55.66, 35.09.

5-amino-3-(4-fluorophenyl)-1-methyl-1H-pyrazole-4-carbonitrile (d). ^1H NMR (400 MHz, $CDCl_3$) & 7.89–7.86 (m, 2H), 7.11 (t, *J* = 8.8 Hz, 2H), 4.55 (s, 2H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) & 162.67 (d, *J* = 244.5 Hz), 153.71, 148.22, 128.68, 128.12 (d, *J* = 8.4 Hz), 116.44, 116.05 (d, *J* = 21.4 Hz), 70.34, 35.19.

5-amino-3-(4-chlorophenyl)-1-methyl-1H-pyrazole-4-carbonitrile (e). ^1H NMR (400 MHz, $CDCl_3$) & 7.84 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 4.46 (s, 2H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) & 151.55, 149.19, 134.92, 129.74, 128.96, 127.46, 115.33, 73.62, 34.81.

5-amino-3-(4-bromophenyl)-1-methyl-1H-pyrazole-4-carbonitrile (f), ^1H NMR (400 MHz, $CDCl_3$) & 7.78 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 4.39 (s, 2H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) & 151.46, 149.22, 131.92, 130.18, 127.71, 123.21, 115.24, 73.72, 34.83.

3. Results and discussion

The XRD patterns of DP-pfa@Fe_2O_3 and pfa@Fe_2O_3 are shown in Fig. 1. From Fig. 1, we can find DP-pfa@Fe_2O_3 and pfa@Fe_2O_3 have similar XRD patterns which correspond to the cubic phase hematite (JCPDS no. 73–0603). The broad peak between 20° and 30° are assigned to amorphous PVP. No other diffraction peaks can be detected, indicating that the introduction of pyrrole-2-carboxylic acid and DP have