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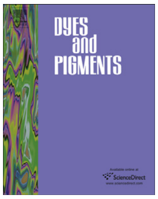

Novel hydrogen bonding composite based on copper phthalocyanine/perylene diimide derivatives p-n heterojunction with improved photocatalytic activity

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ABSTRACT

Among photocatalytic materials, p-n heterojunction-type photocatalysts has good photocatalytic performance under visible light irradiation. Herein, a novel Copper phthalocyanine/perylene diimide derivatives p-n heterojunction photoeatalysts based on the intermolecular hydrogen bond between pyridyl and carboxyl was designed and characterized using FT-IR, UV–vis and photoluminescence spectra, and then compared their photocatalytic performance by degradation for rhodamine B (RhB) under visible light irradiation. The hydrogen bond composites shows significant higher photocatalytic activity comparing with its parent, and the photocatalysis increased with increasing of mole fraction of perylene diimide derivatives. The change of morphology and p-n heterojunction structure are in favor of the high photocatalytic active. Furthermore, the photocatalytic mechanism was investigated by radical scavengers testing, that confirmed hydroxyl radical (•OH) was the main reactive species for the degradation of RhB.

1. Introduction

Photocatalysis, based on its application in environment cleaning, waste water treatment, and water photo-splitting, has gained increasing attention as a promising technique [1–3]. A large amount of photocatalytic materials have been developed, including TiO_2 [4,5], ZnO [6,7], Metallophalocyanine (MPc) [8,9], g-C_3N_4 [10,11] and their composites [12,13]. Among these reported photocatalytic material system, p-n heterojunction-type photoeatalysts are received much attention in photocatalytic researches due to its unique conduction bands and special electron transmission character. For example, p-n heterojunction-type photoeatalysts Bi_2S_3/BiOI [14], WO_3/H_2WO_4 [15], etc. The p-n heterojunction is not only to extend the wavelength range of wide gap semiconductors, but also to suppress the carrier recombination by the built-in electric field, so p-n heterojunction photocatalysis shows high photocatalytic performance compared with the corresponding p type or n type semiconductor materials [16,17]. Up today, p-n heterojunction photocatalysis mainly based on inorganic material system, but few researches has been reported about the p-n heterojunction photocatalysis in the whole organic system.

Metal phthalocyanine compounds (MPcs) have drawn considerable attention as organic photocatalysts for degradation of organic pollutants [18–20]. However, the recombination of photogenerated charges cause an obvious decrease of their photocatalytic performance. An efficient way to suppress the recombination of photogenerated charges were to design p-n heterojunction photocatalysis [21]. Moreover, the MPcs also has been paid more and more attention as an electron donor in the heterojunction solar cells [22,23]. As an air-stable n-type organic semiconductor materials, Perylene diimide and its derivatives (PDIs) are well known electron acceptors with low reduction potential and broad spectral absorption range [24,25]. Therefore perylene diimide should be favorable candidates for use as an electron acceptors in photovoltaic field [26,27]. In addition, all of us know that the organic composite is easily obtained by hydrogen bond or host-guest self assembly, etc [28–30]. For the organic composite based

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on hydrogen bond self-assembly, the hydrogen bond between the carboxylic acid and pyridyl is most stable due to high non valence bond energy between them. A revelation was given to us based on above view, that metal phthalocyanine/perylene diimide hydrogen bonding composite may be a promising materials to improve photocatalytic performance of MPcs.

In this work, the 2,9,16,23-Tetrakis (4′-carboxylatophenoxy) phthalocyanine copper (CuTcPc) and *N*-(3,4,5-three-dodecyloxy-1-amino-phenyl)-*N*′-(4-amino-pyridyl)perylene-3,4,9,10-tetracarboxyc diimide (PDIC12) were designed and synthesized. The PDIC12/CuTcPc hydrogen bonding composites was prepared by self-assembly technology in mixture solution, then their photocatalytic properties were studied via the degradation of rhodamine B under visible light irradiation. Furthermore, various scavengers were introduced to the photocatalytic reaction system to identify the active species in the photocatalytic oxidation process, and the possible photocatalytic mechanisms were investigated and discussed systematically.

2. Experiment section

2.1. Materials and reagents

Rhodamine B, isopropanol (IPA), *p*-benzoquinone (BQ), quinoline, zinc acetate ($Zn(Ac)_2$) potassium iodide (KI) were purchased from Aladdin Chemical Co., Ltd., Sodium carbonate (Na_2CO_3), hydrochloric acid, 4-aminopyridine, 4-Nitrophthalonitrile, 4′-Hydroxybiphenyl-4-carboxylic acid ($C_{13}H_9O_3$), Potassium carbonate (K_2CO_3), cupric bromide and 1-Pentanol were purchased from Xiya Reagent Chemical Co., Ltd., dichloromethane (DCM), quinoline, methanol and *N,N*-Dimethylformamide (DMF) were obtained from Tianjin Kai Tong Chemical Co., Ltd., respectively. All reagents from commercial sources were used without further purification unless otherwise specified. DMF, DCM and 1-Pentanol was fractionally distilled under reduced pressure. The quinoline was purified by 4-A molecular sieves be soaked for 48 h.

2.2. Preparation of PDIC12/CuTcPc

PDIC12 (**S 1**) and CuTcPc (**S 2**) were synthesized according to the literature [31,32]. Scheme 1 shows the (structural changes with addition of PDIC12) preparation process of heterojunction photocatalysis composite PDIC12/CuTcPc. PDIC12 was dispersed in DCM, and then ultrasounded for 2 h. Solution concentration of PDIC12 is 4×10^{-3} mol/L. CuTcPc were dissolved in DMF and ultrasounded for 1 h. Solution concentration of CuTcPc is 2.5×10^{-4} mol/L. PDIC12 solution was added CuTcPc solution (V:V = 1:4), and then ultrasounded for 3 h. The solution was put into oven at 40 °C. With solvent slowly evaporating, we saw flocculent precipitate. The precipitate was dried with in 72 h at 80 °C in vacuum oven. PDIC12/CuTcPc catalyst was obtained. The molar ratio of PDIC12 and CuTcPc is 4:1. The molar ratio of PDIC12 containing the pyridyl with CuTcPc containing the carboxyl is 1:1. So, the PDIC12/CuTcPc catalyst is also entire hydrogen bond composites by (—C—*O*—O—H…N) intermolecular hydrogen bonding. Using the same process, a series of PDIC12/CuTcPc catalysts with different molar ratios of PDIC12 were prepared. The as-prepared photocatalysts were named as PDIC12/CuTcPc (80%) (the molar percentage of PDIC12 of 80%), PDIC12/CuTcPc (66.7%) (the molar percentage of PDIC12 of 66.7%), PDIC12/CuTcPc (50%) (the molar percentage of PDIC12 of 50%), respectively. And the simple mechanical mixture of PDIC12 and CuTcPc was defined as PDIC12 + CuTcPc (80%) (the molar percentage of PDIC12 of 80%).

2.3. Characterization

^{1}H NMR spectra was recorded on Bruker 400 MHz Spectrometer with $CDCl_3$ and DMSO tetramethysilane (TMS) as an internal reference. Infrared measurement with the KBr pellet technique was performed within the 400 - 4000 cm^{-1} on a Perkin Elemer SP100 Fourier transform infrared spectrometer. UV–Vis spectra were measured using a Perkin Elemer Lambda 35. Fluorescence spectra (PL) were recorded on a Perkin Elmer RF-5301PC spectraphotometer. The morphology of the PDIC12/CuTcPc, CuTcPc and PDIC12 were observed by scanning electron microscopy (SEM, Hitachi S4800 II). Cyclic voltammetry measurement were performed in solution, under argon atmosphere with a computer controlled CHI600d electrochemical workstation in a three electrode single compartment cell using platinum electrodes and Ag^+/AgCl electrode as the reference electrode, with Fc/Fc* redox couple as internal standard, with a tetrabutyl-ammonium hexafluoro phosphate (Bu_4NPF_6) solution (0.1 M) in DMF at a scan rate of 0.1 V/s [33].

2.4. Photocatalytic experiments

The photocatalytic performance of PDIC12/CuTcPc was conducted in a glass sample beaker with side irradiation provided by a 100 W Xe lamp (Beijing China Education Au-light Co., Ltd.). A UV cutoff filter (Beijing China Education Au-light Co., Ltd.) was employed to filter the UV light (<400 nm) to ensure illumination by visible light only. CuTcPc (0.5 g/L), PDIC12/CuTcPc (80%) (0.5 g/L), PDIC12/CuTcPc (66.7%) (0.5 g/L), PDIC12/CuTcPc (50%) (0.5 g/L), PDIC12 + CuTcPc (80%) (0.5 g/L) and PDIC12 (0.5 g/L) was dispersed in RhB aqueous solution (1.5×10^{-5} mol/L) and the photocatalytic experiment was carried out at 20 °C and atmospheric pressure. Before irradiation, the suspension was stirred in the dark for 2 h to establish adsorption-desorption equilibrium of RhB on the catalysts. Before irradiation, the suspension was treated by ultrasonication for 10 min. The experiment temprature was controlled by low-temprature cooling liquid circulating pump (Shanghai Yikai Instrument Equipment Co., Ltd.). The distance between the lamp and reactor containing RhB solution was about 18 cm. At given time intervals, the solution was continually taken from the reactor. The concentration of RhB was determined by UV–vis spectrometer at 554 nm.

Photoelectrochemical test with a ChI650E electrochemical system (China) was carried out in a conventional three electrodes, The ITO/photocatalyst electrode served as the working electrode. A Pt wire served as the counter electrode and Ag/AgCl (saturated KCl) served as a reference electrode. The working electrodes were prepared as follows: photocatalyst was added into the mixed solution of DMF and DCM, then the obtained slurry was dip-coated onto the surface of the ITO with a size of 1 × 2 cm and dried at 70 °C.

3. Result and discussion

FT-IR spectra of the PDIC12/CuTcPc, PDIC12 and CuTcPc were shown in Fig. 1. In contrast with two parents, the observed IR spectra of PDIC12/CuTcPc shows a superposition of signal for two parents. Furthermore, the most significant change in FT-IR spectra of PDIC12/CuTcPc appeared at 2443 cm^{-1}, which is assigned to the stretching vibration of O—H group of the carboxylic acid in the hydrogen-bonded state of carboxyl-pyridyl units [34–37]. Further evidence for PDIC12/CuTcPc hydrogen bonding composites comes from disappearance of the stretching vibration absorption peak of in the association state carboxyhydroxyl at around 3000 cm^{-1} broad peak. These results indicate the formation of the PDIC12/CuTcPc hydrogen bonding composites.