Short Communication

Efficient photo-degradation of 4-nitrophenol by using new CuPp-TiO₂ photocatalyst under visible light irradiation

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Abstract

A new functionalized porphyrin, 5-mono-[4-(2-(4-acetateethyl)-phenoxy) ethoxy]-10, 15, 20-triphenylporphyrin H₂Pp (1) and its copper (II) porphyrin (CuPp) were synthesized. The corresponding CuPp-TiO₂ photocatalyst was then prepared and characterized by means of FT-IR and diffused reflectance spectra, X-ray diffraction (XRD). The photocatalytic activity of CuPp-TiO₂ was investigated by testing the photo-degradation of 4-nitrophenol (4-NP) in aqueous solution under visible light irradiation with the assistance of appropriate amount of H₂O₂. The results indicated that the photo-degradation of 4-NP was much enhanced compared with the bare TiO₂. Additionally, a possible mechanism of the photocatalytic degradation was also proposed in the presence of H₂O₂ under visible light irradiation.

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1. Introduction

As an economical and environment-friendly method for the treatment and purification of polluted water, photocatalysis has been attracted much attention for the application to environmental problems in recent years [1–3]. Among various photocatalysts, titanium dioxide (TiO₂) is believed to be one of the most promising photocatalysts in terms of environmental application owing to its nontoxic, good chemical stability and high photocatalytic activation [4–7]. However, being a wide band-gap (Eg = 3.2 eV for anatase), TiO₂ is active only upon irradiation of UV light (λ < 387.5 nm) [8–9].

To solve this issue, different approaches have been devoted to enhancing the photocatalytic activity of TiO₂ in which the response of the semiconductor was extended towards the visible region. Among them, the porphyrin-sensitized TiO₂ system has been proposed for the photodegradation of various kinds of organic pollutants in aqueous suspension [10–12]. However, few researches have been found for the photo-degradation of 4-NP under visible light irradiation in the presence of H₂O₂.

Based on our previous work [13, 14], a new functionalized porphyrin complex, 5-mono-[4-(2-(4-acetateethyl)-phenoxy) ethoxy]-10,15,20-triphenylporphyrin H₂Pp (2) and its corresponding copper complex were synthesized and characterized in this communication (Fig. 1). The CuPp-TiO₂ photocatalyst was then prepared and characterized by XRD, FT-IR, DRS. As well as the further photocatalytic activity of the CuPp-TiO₂ was investigated via the photo-degradation of 4-nitrophenol (4-NP) in aqueous suspension under visible light irradiation in the presence of H₂O₂. Moreover, a possible mechanism of the photo-degradation of 4-NP under visible light irradiation was also proposed.

2. Experimental

2.1. Reagents and materials

Reagents and solvents were purchased from Tianjin Chemical Reagents Company. They were used without further purification except pyrrole and DMF, which were distilled before use. 5-mono-(4-bromoethoxy)-10,15,20-triphenylporphyrin H₂Pp (1) was synthesized according to literature [15]. TiO₂ was purchased from Acros Organics, U.S.A. (anatase phase, BET specific surface area 9 m²/g), using in preparation of loaded samples applied as photocatalyst in photo-reactivity experiments.

2.2. Equipment

Model XPA-VII photocatalytic reactor (Xujiang Electromechanical Plant, Nanjing, China) was employed to evaluate for the photo-degradation of 4-NP. Elemental analysis(C, H and N) was performed by Vario EL-III CHNOS instrument. FT-IR spectra were recorded on A BEQUIZNDX-550 using the KBr pellet technique. UV–vis spectra were recorded by a Shimadzu UV-1800 UV–vis-NIR spectrophotometer.
1H NMR spectra were recorded at room temperature using a Varian Inova 400 MHz apparatus and tetra-methylsilane (TMS) for reference. Mass spectrometry (MS) analysis was carried out on a matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS, Krato Analytical Company of Shimadzu Biotech, Manchester, Britain) using a standard procedure involving 1 mL of the sample solution. The X-ray diffraction (XRD) measurement was performed with a Bruker D8 diffractometer using graphite monochromatic copper radiation (Cu Kα) at 40 kV, 30 mA over the 2θ range 20–80°.

2.3. Synthesis of porphyrin and copper porphyrin

2.3.1 5-mono-[4-(2-(4-acetateethyl)-phenoxy)ethoxy]-10,15,20-triphenylporphyrin H2Pp (2)

The compound H2Pp (1) (0.068 mmol, 0.05 g) was dissolved in distilled DMF (10 mL) with a large excess of anhydrous K2CO3 (0.15 g), then ethyl-4-hydroxybenzoate (0.2564 g, 1.3556 mmol) was added and the solution was stirred at 60 °C for 48 h. The process of the reaction was monitored by TLC. After purifying with dichloromethane/ethyl acetate=10/1 to give H2Pp (2) as a purple solid. Yield: 38%. Mp: >250 °C, Anal. Calcd. for C55H42N4O4 (mol.wt: 822.95), %: C, 80.25(80.27); H, 5.09(5.14); N, 6.83(6.81). MS: m/z 822.53 ([M+H]+ amu. UV−vis(CH2Cl2): λmax nm, 415 (Soret band), 539 (Q bands). FT-IR: υ cm−1, 2924, 2855, 1711, 1605, 1507, 1425, 1235, 1106, 1069, 965, 798, 701. 1H NMR(CDCl3, 400 MHz): δ ppm 8.87 (s, 8H, Ar), 7.74 (m,11H, Ar), 7.29 (d, J = 8.40 Hz, 2H, Ar), 7.07 (d, J = 8.76 Hz, 2H, Ar), 4.56 (t, J = 4.86 Hz, 2H, CH2), 2.79 (br s, 2H, NH).

2.3.2. Cu(II) 5-mono-[4-(2-(4-acetateethyl)-phenoxy)ethoxy]-10,15,20-triphenylporphyrin CuPp

The general procedure for the synthesis of CuPp has been described in our previous work [13]. CuPp yield: 92%. Mp: >250 °C, Anal. Calcd. for C57H42CuN4O4 (mol.wt: 884.43), %: C, 75.31(74.69); H, 4.35(4.56); N, 6.82(6.33). MS: m/z 886.75 ([M + H]+) amu. UV−vis(CH2Cl2): λmax nm, 415 (Soret band), 539 (Q bands). FT-IR: υ cm−1, 2923, 2855, 1711, 1605, 1504, 1448, 1236, 1105, 1069 and 799.

2.4. Preparation of CuPp-TiO2 photocatalyst

An amount (6 μmol) of the CuPp was dissolved in 30 mL CH2Cl2 and 1 g TiO2 was added to the solution. The suspension was stirred for 5 h at the room temperature. Then the solvent was removed under vacuum and the photocatalyst was collected.

2.5. Photocatalytic degradation

The photoreactivity experiments for 4-NP photo-degradation were carried out by using a Model XPA-VII photocatalytic reactor of cylindrical shape, the central light source was 400 W the halogen lamp placed in a quartz socket tube with one end closed. The distance between the light source and the reactor was 12 cm and the average light intensity at the position of the sample surface was about 609 mw·cm−2. The temperature inside the reactor was maintained at ca. 25 °C by means of a continuous circulation of water in a jacket surrounding the reactor. A 400 nm cutoff filter was employed between the lamp and the reactor for visible light photo-degradation.

The reacting suspension consisting of 50 mL of 1 × 10−4 mol/L 4-NP and 10 mg of photocatalyst was magnetically stirred and had air bubbled into the suspension for 30 min before switching on the lamp and an amount of H2O2 (1 mL) was added into the suspension. The photo-degradation lasted 160 min, and samples of 3 mL was withdrawn from the suspension every 20 min during the irradiation. The photo-degradation ratio was determined using a spectrophotometer and the absorbance at 317 nm was recorded.

3. Results and discussion


The target porphyrin H2Pp (2) was synthesized through substituting bromine atom in H2Pp (1) by ethyl-4-hydroxybenzoate as shown in Scheme 1 and its copper porphyrin was obtained almost quantitatively.

The UV−vis spectrum of H2Pp (2) consists of a Soret band at 418 nm, and Q bands at 484, 515, 550 and 591 nm. The Soret band for CuPp appears at 415 and the Q bands at 539 nm. The coordination of Cu(II) ion to the porphyrin caused blue shift of Soret band as well for a decreasing number of Q bands. Mass spectroscopy data of the H2Pp (2) and its CuPp perfectly correspond to the expected [M + H]+ m/z values. The main change of the FT-IR spectrum of CuPp compared with H2Pp (2) is the disappearance of stretching vibration of N–H. Besides, 1H NMR spectrum of H2Pp (2) was also consistent with the structure. These spectroscopy data are well consistent with the structure of the synthesized porphyrin and its corresponding copper porphyrin.

3.2. Solid diffuse reflection UV−vis spectra

As shown in Fig. 2, the diffuse reflection spectra of the bare TiO2 and CuPp-TiO2 photocatalyst were recorded in the range of 350–750 nm. Obviously, there is no absorption above 400 nm for bare...
\[ \text{CuPp-TiO}_2 \] whereas the \text{CuPp-TiO}_2 photocatalyst exhibits the feature peaks of CuPp observed in CH\textsubscript{2}Cl\textsubscript{2} solution, which indicated that CuPp successfully loaded onto the \text{TiO}_2 surface with integrated porphyrin framework. Consequently, \text{CuPp-TiO}_2 photocatalyst exhibits a broader absorption range for the solar spectrum than \text{bare TiO}_2. Significantly, it is noticed that the Soret and Q band of the \text{CuPp-TiO}_2 are all red-shifted and broadened relatively to CuPp observed in CH\textsubscript{2}Cl\textsubscript{2} solution, implying that there exists a weak interaction between \text{TiO}_2 and its corresponding copper porphyrin.

3.3. FT-IR spectra of photocatalyst

The bare \text{TiO}_2 and \text{CuPp-TiO}_2 photocatalyst were identified by FT-IR spectroscopy (Fig. 3). For bare \text{TiO}_2, the vibrations at 3425 cm\(^{-1}\) and 1631 cm\(^{-1}\) observed correspond to the stretching vibrations and bending vibration of \(-\text{OH}\) on the surface of \text{TiO}_2, respectively. It is indicated that there contain a great deal of hydroxyls in the \text{TiO}_2, which is essential for the linking of CuPp on the \text{TiO}_2. When CuPp is adsorbed on \text{TiO}_2, the main characteristic vibrations attributed to the C-C and C-H of CuPp can be observed, which indicate that the \text{TiO}_2 modified by CuPp has been achieved. More importantly, in the FT-IR of \text{CuPp-TiO}_2, the vibration attributed to \(\nu_{\text{C-O-C}}\) is located at 1243 cm\(^{-1}\), which is blue-shifted 7 cm\(^{-1}\) relative to that of CuPp. Further observation shows that the peaks corresponding to the stretching vibrations of hydroxyl groups in \text{CuPp-TiO}_2 photocatalyst become narrower and weaker, indicating the decrease of hydroxyl groups on \text{TiO}_2 surface, which is due to the interaction between \(-\text{OH}\) and CuPp after loading process.

3.4. XRD characterization of \text{CuPp-TiO}_2 photocatalyst

XRD was employed to investigate the crystal identity of \text{TiO}_2 samples and the effect of CuPp on the crystal structure of \text{TiO}_2. Fig. 4 displays XRD patterns for the bare \text{TiO}_2 and \text{CuPp-TiO}_2 photocatalyst. No differences were found in the two samples, and the prominent diffraction peaks at 25.3°, 37.8°, 48.0°, 54.0°, 62.7°, 68.8°, 70.3° and 75.1° were observed which were attributed to anatase \text{TiO}_2 [16]. The result indicated that the CuPp loaded onto the surface of \text{TiO}_2 hardly has any effect on the crystal structure of \text{TiO}_2 powders.

3.5. Photocatalytic activity of photocatalyst

The photocatalytic activities for the photo-degradation of 4-nitrophenol in aqueous suspension under visible light irradiation in the presence of H\textsubscript{2}O\textsubscript{2} using prepared photocatalyst were tested. Obviously, as shown in Fig. 5, \text{TiO}_2 (curve c) alone cannot drive the direct photocatalysis under visible light irradiation, H\textsubscript{2}O\textsubscript{2} (curve b) displays much lower photocatalytic activity when compared to \text{TiO}_2/H\textsubscript{2}O\textsubscript{2} (curve d). However, the remarkable enhancement of photocatalytic activity is presented for \text{CuPp-TiO}_2/H\textsubscript{2}O\textsubscript{2} (curve e). For comparison, the photocatalytic activity of \text{CuPp}(5b)-\text{TiO}_2 reported by us previously [14] is also tested under the same condition and given in Fig. 5 (curve f). The two photocatalysts display the closely photoactivity and much enhanced photocatalytic activity than bare \text{TiO}_2. Meanwhile, the time of photocatalytic reaction is greatly shortened compared with our previous work [14]. These results indicate that the photocatalytic activities of \text{CuPp-TiO}_2 are significantly enhanced in the presence of H\textsubscript{2}O\textsubscript{2} under visible irradiation. As it is well known, hydrogen peroxide is widely used as a good electron acceptor in the photo-degradation of organic pollutant reactions [17]. It has been found that an increase in the concentration of H\textsubscript{2}O\textsubscript{2} led to an increase of \(\bullet\text{OH}\) radicals available to accelerate the photo-degradation.

3.6. Photocatalytic degradation mechanism of 4-NP under visible light

Under visible light irradiation, the process of \text{CuPp-TiO}_2 photocatalytic reaction can be intrigued by the excitation of ground state of the sensitizer [CuPp] via one photon transition \((h\nu)\) to its excited state \text{TiO}_2[CuPp]\(^*\) (Eq. (1)). Then the photo-induced electrons inject into the conduction band (CB) of \text{TiO}_2, and thus the reactive electrons on the CB of \text{TiO}_2 initiate the decomposition of H\textsubscript{2}O\textsubscript{2}(Eqs. (2) and (3)), it can give rise to the generation of hydroxyl radicals (\(\bullet\text{OH}\)), which has potential to photo-degrade 4-NP into small molecules or H\textsubscript{2}O (Eq. (5)). What’s more, H\textsubscript{2}O\textsubscript{2} is essential probably to
Conclusion

In summary, the new porphyrin H_{3}Pp (2) and its CuPp have been described along with the corresponding CuPp-TiO_{2} photocatalyst. The XRD and FT-IR spectra demonstrated that CuPp was successfully loaded onto the surface of TiO_{2} microsphere and did not influence the phase and surface state of TiO_{2}. There exists a weak interaction between TiO_{2} surface and copper (II) porphyrin. Under the visible light irradiation, the CuPp-TiO_{2} photocatalyst in the presence of H_{2}O_{2} was highly effective for the photo-degradation of nonbiodegradable 4-NP. The new photocatalyst CuPp-TiO_{2} showed much enhanced photoactivity than bare TiO_{2}. Moreover, a possible reaction mechanism has been discussed.

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References