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Efficient visible photodegradation of 4-nitrophenol in the presence of H_2O_2 by using a new copper(II) porphyrin–TiO₂ photocatalyst

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ABSTRACT

A new imidazolyl-linked pophyrin, 5-[4-(2-imidazolyl)ethoxyl]phenyl-10,15,20-triphenylporphyrin and its copper(II) porphyrin were synthesized and characterized spectroscopically. The CuPp–TiO₂ photocatalyst was also prepared and characterized by means of high-resolution transmission electron microscopy (TEM), X-ray diffraction (XRD), UV–vis spectra and FT-IR spectra. The photocatalytic activity was investigated by photodegradation of 4-nitrophenol (4-NP) in aqueous solution with a small amount of H_2O_2 under visible light irradiation ($\lambda > 400$ nm). The results indicated that H_2O_2 can enhance greatly the visible photocatalytic activity of CuPp–TiO₂ photocatalyst. Additionally, a possible mechanism of the photocatalytic degradation was proposed.

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1. Introduction

 TiO_2 has received a lot of attention as a promising semiconductor photocatalyst because of its nontoxicity, low cost, chemical stability, and high catalytic activity [1,2], but the wide band gap of TiO_2 (3.2 eV for the anatase structure) restricts its photocatalytic applications to the UV range. Therefore, improving the visible photocatalytic activity of TiO_2 -base photocatalyst for taking full advantage of the main part of the solar spectrum becomes an important and challenging issue. Various approaches have been attempted to enhance the visible-light utilization of TiO_2 including surface modification, doping, sensitizations and semiconductor coupling [3–10].

Porphyrins are a kind of excellent photosensitizers which have large π -electron conjugate systems and high absorption coefficient within the solar spectrum. The porphyrin-sensitized TiO₂ system has been proposed firstly by Mele for the oxidative degradation of 4-nitrophenol in water [4]. It has been verified that porphyrins–TiO₂ can degrade the organic molecules in aqueous solutions efficiently using the solar energy. Some porphyrins and metalloporphyrins have been explored to improve the photocatalytic performance of TiO₂ on the degradation of organic pollutants [11,12]. These results showed that porphyrin modified TiO₂ photocatalysts exhibited higher photoactivity than bare TiO₂ under UV light irradiation [13–16]. However, under visible light irradiation, the photocatalytic efficiencies of all photocatalysts decreased evidently compared with those in UV light condition [17,18].

In order to improve the visible-light-driven photocatalytic efficiency of porphyrin modified TiO_2 photocatalyst, it is necessary to explore the influential factors of the efficiency of porphyrin– TiO_2 systems by adding other oxidants such as H_2O_2 except oxygen.

For this purpose, a new imidazolyl-linked porphyrin as well as its copper porphyrin was synthesized in this paper (Fig. 1). The imidazolyl-linked porphyrin was selected because the nitrogen atom of imidazole can coordinate to titanium atom of the surface of TiO₂, which benefits the electronic transfer from porphyrin to TiO₂ and thus increase the photocatalytic activity. In addition, in our previous research, we find the central coordinated metal ion in the porphyrins ring plays a critical role in the photocatalytic processes of the porphyrin-TiO₂ system, and copper porphyrin-TiO₂ photocatalyst displays the most significant improvement on photoactivity [18]. Therefore, we prepared and characterized a new CuPp-TiO₂ photocatalyst by using synthesized imidazolyl-linked copper porphyrin and investigated its photocatalytic efficiency on the degradation of 4-notrophenol (4-NP) in the presence of H_2O_2 under visible light irradiation ($\lambda > 400$ nm). Moreover, a possible photocatalytic mechanism was also proposed.

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Fig. 1. The structure of porphyrin and its copper(II) porphyrin.

2. Experimental

2.1. Reagents and materials

Reagents were obtained from Beijing Chemical Reagents Company. They were used directly after received except pyrrole, which was distilled before use. TiO_2 was purchased from Acros Organics, USA (anatase phase, BET specific surface area $9 \text{ m}^2/\text{g}$), using in preparation of loaded samples applied as photocatalyst in photoreactivity experiments. 5-(4-hydroxyphenyl)-10,15,20triphenylporphyrin (1) was synthesized according to a reported procedure [19].

2.2. Equipment

Elemental analyses (C, H and N) were performed by Vario EL-III CHNOS instrument. FT-IR spectra were recorded on a BEQ UZNDX-550 spectrometer on samples embedded in KBr pellets. UV-vis spectra were performed by Shimadzu UV1800 UV-vis-NIR spectrophotometer. ¹H NMR spectra were recorded by using a Varian Inova 400 MHz apparatus at room temperature and tetramethylsilane (TMS) for reference. Mass spectrometry (MS) analyses were 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). 1 μ L of sample solution and of the matrix mixture were spotted into wells of the MALDI sample plate, and air-dried. The samples were analyzed in the linear ion mode with CHCA as matrix. External calibration was achieved using a standard peptide and protein mix from Sigma.

Diffuse reflectance (DR) spectra were obtained at room temperature in the wavelength range 200–800 nm using a Shimadzu UV-2401PC spectrophotometer with BaSO₄ as reference material. The surface morphologies of the samples were analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi-S4800) with energy dispersive spectrometry (EDS, Quanta 400FEG) and high-resolution transmission electron microscope (TEM, JEOL JEM-3010). The X-ray diffraction measurement was performed with a Bruker D8 diffractometer using graphitemonochromatic copper radiation (Cu K α) at 40 kV, 30 mA over the 2 θ range 20–80°.

2.3. Synthesis of porphyrin and copper porphyrin

2.3.1.

5-(4-(2-Bromoethoxyl)phenyl)-10,15,20-triphenylporphyrin (2)

1,2-Dibromoethane (1.80 g, 9.60 mmol) and potassium carbonate (0.40 g, 2.89 mmol) were dissolved in dry N,N-dimethylformamide (15 mL), and compound **1** (0.20 g, 0.32 mmol) was added. Then the solution was stirred under nitrogen for 8 h at 80 °C. The process of the reaction was monitored by TLC. Then the solvent was removed under vacuum and the crude product was purified by chromatography on a silica gel column with CH_2Cl_2 as eluent to afford a purple solid.

Yield: 60%. Mp: >250 °C, Anal. calcd. (found) for $C_{46}H_{33}BrN_4O$ (mol. wt: 737.6), %: C, 74.93 (74.90); H, 4.58 (4.51); N, 7.61 (7.59). MS: m/z 737.38 (calcd. for [M+H]⁺ amu). UV–vis (CH₂Cl₂): λ_{max} /nm, 418 (Soret band), 515, 551, 591, 647 (Q-bands). FT-IR: ν , cm⁻¹, 3319, 3054, 2921, 1600, 1470, 1240, 1217, 1072, 965, 800, 702, 551.

2.3.2. 5-[4-(2-imidazolyl)-ethoxyl]phenyl-10,15,20-triphenylporphyrin (**3**)

A mixture of compound **2** (0.10 g, 0.13 mmol), anhydrous K_2CO_3 (0.50 g, 3.60 mmol) and imidazole (0.90 g, 13 mmol) in dry dimethylformamide (15 mL) was stirred for 24 h at room temperature. The process of the reaction was monitored by TLC. The unreacted solid salt was filtered and the solvent was removed under vacuum, then the residue was dissolved in CHCl₃ (40 mL) and washed with H₂O to remove unreacted imidazole. After concentrating via rotary evaporation, the residue was chromatographed on a silica gel column using CHCl₃ first and then CHCl₃: CH₃CH₂OH = 10:1 (v:v) as eluent. The main purple band was collected.

Yield: 40%. Mp: >250 °C. Anal. calcd. for $C_{49}H_{36}N_6O$ (mol. wt: 724.3), %: C, 82.21 (81.19); H, 5.08 (5.03); N, 11.63 (11.59). MS: *m/z* 725.34 (calcd. for [M+H]⁺ amu). UV–vis (CH₂Cl₂) λ_{max}/nm , 417 (Soret band), 515, 550, 590, 646 (Q-band). FT-IR: ν , cm⁻¹, 3318, 3056, 2924, 1601, 1506, 1471, 1349, 1244, 1108, 1076, 964, 802, 734, 700. ¹H NMR (400 MHz, CDCl₃): δ in ppm = 8.84–8.81 (d+d, 8H, β position of the pyrrolemoiety), 8.20 (d, *J* = 6.8 Hz, 8H), 7.75–7.73 (m, 11H), 8.07 (s, 1H), 7.71 (s, 1H), 7.12 (s, 1H), 4.36 (t, 3H), 4.31 (t, 3H), -2.78 (s, 2H).

2.3.3. Cu(II) 5-[4-(2-imidazolyl)-ethoxyl]phenyl-10,15,20triphenylporphyrin CuPp (**4**)

CuCl₂ (20.7 mg, 0.15 mmol) were added to H_2Pp (3) (36.2 mg, 0.05 mmol) dissolved in a mixture of 15 mL CH₂Cl₂ and CH₃CH₂OH (7 mL). The mixture was stirred for 24 h at room temperature and monitored by TLC until the starting material H_2Pp (3) disappeared. The unreacted solid salt was filtered and the solvent was removed under vacuum. The crude product was purified by chromatography on a silica gel column with CH₂Cl₂ as eluant. **CuPp** (4) was obtained in nearly quantitative yield.

Yield: 93%. Mp: >250 °C. Anal. calcd. for CuC₄₉H₃₄N₆O (mol. wt: 786.3), %: C, 74.91 (74.84); H, 4.29 (4.36); N, 10.75 (10.69). MS: *m*/*z* 787.21 (calcd. for [M+H]⁺ amu). UV–vis (CH₂Cl₂) λ_{max} /nm. 414 (Soret-band), 539 (Q-band). FT-IR: ν , cm⁻¹, 2922, 1601, 1500, 1471, 1349, 1237, 1107, 1074, 997, 801, 701.

2.4. Preparation of the CuPp–TiO₂ photocatalyst

The loaded sample used as photocatalyst for the photodegradation experiments was prepared as follows: an amount (6μ mol) of **CuPp** (4) was dissolved in 30 mL CH₂Cl₂ and 1 g of finely ground TiO₂ was added to the solution. The suspension was stirred for 5 h



Scheme 1. Synthesis of the porphyrin H₂Pp and copper(II) porphyrin CuPp.

at room temperature. Then the solvent was removed under vacuum and the photocatalyst was collected [20].

2.5. Photodegradation setup and photodegradation experiments

The photodegradation experiments have been conducted using Model XPA-II photocatalytic reaction instrument (Nanjing Xujiang Electromechanical Factory): central light source was 400 W halogen lamp placed in a quartz socket tube with one end closed. The system was cooled by circulating water running through an interlayer and magnetic agitation was used so that catalyst can suspend in the reaction solution. The temperature of the reactor was maintained at the constant temperature water bath (25 ± 1 °C), which was fixed on the base of the apparatus. A cutoff filter of 400 nm wavelength was placed between the lamp and the reactor to ensure that photocatalysis was irradiated by visible light only.

The reacting suspension consisting of $50 \text{ mL } 10^{-4} \text{ mol/L } 4\text{-NP}$ and 10.0 mg catalysts was magnetically stirred. Air was bubbled into the suspension for 30 min before switching on the lamp. Samples of 3 mL were withdrawn from the suspension every 20 min during the irradiation. The photocatalysts were separated from the solution by centrifugation and the quantitative determination of 4-NP was performed by measuring its absorption at 317 nm with a Shimadzu UV1800 UV-vis-NIR spectrophotometer.

3. Results and discussion

3.1. Synthesis of the porphyrins H₂Pp and CuPp

The synthetic route of the porphyrin and copper(II) porphyrin was illustrated in Scheme 1. The porphyrin **2** was synthesized in 60% isolated yields, by displacement reaction of 1,2-dibromoethane with 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (1) in DMF in the presence of K₂CO₃. The porphyrin **3** was synthesized by using of porphyrin **2** reacting with imidazole in DMF in the presence of K₂CO₃ with yield of 40%. Successively, the **CuPp** (**4**) was obtained by the reaction of free porphyrin **H₂Pp** (**3**) with excess CuCl₂ in CH₂Cl₂/C₂H₅OH with yields about 90%.

The compounds **H**₂**Pp** (**3**) and **CuPp** (**4**) were characterized by ¹H NMR, UV–vis, FT-IR and MS. The UV–vis spectrum of **H**₂**Pp** (**3**)

showed a band centered at 417 nm (Soret band), and the Q bands absorptions at 515, 550, 590 and 646 nm, respectively. The insertion of Cu(II) into the porphyrin ring caused violet shift of 3 nm of the corresponding Soret band as well as a decreasing number of Q bands in UV–vis spectrum, which due to the increase of the symmetry of porphyrin ring when the hydrogen ions of N–H was replaced by Cu(II). Mass spectroscopy data of **3** and **4** perfectly corresponded to the expected $[M+H]^+$ m/z values. ¹H NMR spectrum was also consistent with the structure of the isolated **3**. The main change of the IR spectrum of copper porphyrin (**4**) compared with free base porphyrin (**3**) was the disappearance of stretching vibration of N–H.

3.2. Morphology of CuPp-TiO₂ photocatalyst

The surface morphologies of TiO₂ and CuPp-TiO₂ photocatalyst can be seen from the SEM images (Fig. 2(a) and (b)). It can be observed that the microspheres of CuPp-TiO₂ have a similar surface condition with bare TiO₂, indicating that the TiO₂ morpha basically are no change before and after loaded with the copper(II) porphyrin. Fig. 2(c)-(f) shows typical TEM images of bare TiO₂ and CuPp-TiO₂ photocatalyst. As was expected, after modification with CuPp, the size of TiO₂ has no obvious change compared with bare TiO_2 (Fig. 2(c) and (d)). From the further observations of the amplified image of CuPp–TiO₂ microsphere (Fig. 2(f)), we find that some nanometer CuPp particles disperse on the surface of TiO₂, while nanometer particles were not found on the surface of bare TiO₂ (Fig. 2(e)), indicating that CuPp is well distributed on the surface of TiO₂. In addition, The EDS results (Fig. 3) of the CuPp-TiO₂ photocatalyst demonstrate that Cu element is present on the surface of TiO₂ microsphere, which probably derived from **CuPp** (4). Therefore, it can be concluded that CuPp is well loaded on the surface of TiO₂ as the small solid particles.

3.3. Diffuse reflectance spectra

Fig. 4 shows the diffuse reflectance spectra of the bare TiO_2 and $CuPp-TiO_2$ photocatalyst recorded in the range of 300–750 nm. Obviously, there is no absorption above 400 nm for bare TiO_2 , while $CuPp-TiO_2$ exhibits the feature peaks observed in CH_2Cl_2 solution, indicating that copper porphyrin **4** successfully loaded onto the TiO_2 surface with maintaining the porphyrin structure framework.



Fig. 2. SEM images (a, b) and TEM images (c-f) of bare TiO₂ (a, c, e) and CuPp-TiO₂ (b, d, f).



Fig. 3. EDS spectrum of CuPp–TiO₂ photocatalyst.



Fig. 4. The diffuse reflectance spectra of bare TiO_2 and $CuPp-TiO_2$ photocatalyst.

Simultaneously, it is noticed that the DR spectrum of $CuPp-TiO_2$ have a significant red shift compared with the spectrum of CuPp



Fig. 5. FT-IR spectra of bare TiO₂ and CuPp-TiO₂ photocatalyst.

in CH_2Cl_2 solution (5 nm red shift of Solet band), which can be attributed to an interaction between TiO_2 and copper porphyrin molecules.

3.4. FT-IR spectra

Fourier transform infrared (FT-IR) technique was used to gain further information about the interaction between CuPp and the surface of TiO₂. Fig. 5 shows the bonding characteristics of functional groups in bare TiO₂ and CuPp–TiO₂ photocatalyst. Obviously, the absorption peak at 3421 cm⁻¹ was associated with the stretching vibrations of surface hydroxyl groups TiO₂, whereas the band around 1643 cm⁻¹ was attributed to the bending vibration of H–OH groups and Ti–OH bond for bare TiO₂ and CuPp–TiO₂, respectively.

The stretching vibrations of C–-C, C–-H bonds can be observed in CuPp–TiO₂ photocatalyst, indicating the existence of copper porphyrin molecules on the surface of TiO₂. Further observation shows that the peaks at 3421 cm⁻¹ become narrower and weaker in CuPp–TiO₂ photocatalyst than that in bare TiO₂, reflecting the decrease of hydroxyl groups after the CuPp was loaded on the surface of TiO₂. It implies that, maybe there exist some reactions between CuPp and the surface of TiO₂.

3.5. XRD patterns

XRD was carried out to investigate the effect of copper porphyrin on the crystal structure of TiO₂. Fig. 6 shows the XRD patterns of the bare TiO₂ and CuPp–TiO₂ photocatalysts. No differences were found in CuPp–TiO₂ photocatalysts and bare TiO₂, and the prominent diffraction peaks at 25.5°, 37.5°, 47.7°, 53.4° and 62.8° were observed which were attributed to anatase TiO₂ [21]. These results indicated that the **CuPp** (**4**) which loaded on the surface of TiO₂ microsphere had no effect on the crystal structure of TiO₂ powders.

3.6. Photocatalytic degradation experiments

Oxygen was bubbled into all the photocatalytic reaction suspensions except the one with nitrogen. The photocatalytic activity of CuPp–TiO₂ photocatalyst was evaluated by the degradation of 4-nitrophenol (4-NP) in water under visible light irradiation (λ > 400 nm) and UV light irradiation. In order to compare and explain the photocatalytic mechanism, other photocatalytic experiments were also performed under different conditions, as shown in Fig. 7.



Fig. 6. XRD patterns of the bare TiO₂ and CuPp–TiO₂ photocatalyst.

3.6.1. Visible-light-driven photocatalytic activity of CuPp-TiO₂

Experimental conditions: $[H_2O_2] = 0.12 \text{ mol/L}$, visible light, $\lambda > 400 \text{ nm}$.

Fig. 7 shows the photodegradation of 4-NP under different experimental conditions. According to previous studies [22,23], $O_2^{\bullet-}$ is mainly formed in the present reaction system under visible light irradiation in the absence of H_2O_2 . The result shows clearly that only a small degradation of 4-NP was obtained under the condition of CuPp-TiO₂/O₂ (curve b), indicating that 4-NP cannot be oxidized by $O_2^{\bullet-}$ effectively within a short time. Hence, to degrade 4-NP effectively using CuPp-TiO₂ photocatalyst under visible light irradiation, hydrogen peroxide was added to the aqueous suspensions. The result shows that almost a complete degradation was obtained within 160 min of visible light irradiation (curve g). However, no degradation of 4-NP was observed by using bare TiO₂ (curve a) and only a small part of 4-NP was degraded by H_2O_2 or TiO₂/H₂O₂ in the absence of CuPp-TiO₂ photocatalyst (curves c and d).

The CuPp–TiO₂ photocatalyst also shows high photocatalytic efficiency under UV light irradiation (curves h and i). A small increase of photocatalytic activity is observed in the presence of H_2O_2 . This due to the hydroxyl radicals (•OH) produced directly by H_2O_2 under the UV light irradiation. Comparing with the results from UV light irradiation, the visible photocatalytic activity of CuPp–TiO₂ has been improved greatly when an appropriate amount of H_2O_2 were added to the suspensions.

To understand the role of •OH on the degradation of 4-NP, the mannitol (a scavenger of hydroxyl radicals [23]) was added into



Fig. 7. 4-NP concentration vs irradiation time using CuPp-TiO₂ photocatalyst.

0

oxidation products



Fig. 8. The effection of H₂O₂ concentration on degradation of 4-NP.

CuPp–TiO₂ suspended aqueous (curve e). Obviously, it affected the degradation of 4-NP greatly, because the hydroxyl radicals were consumed by mannitol and consequently lead to a low degradation of 4-NP. The result suggests that hydroxyl radicals were predominantly formed in the reaction system.

To assess the role of dissolved O_2 during the photocatalytic degradation process, N_2 was bubbled to remove O_2 from the aqueous suspensions. In this condition, a small decrease of degradation was occurred (curve f) compared with the one under the presence of oxygen (curve g). The result indicates that the effect of O_2 on the photodegradation of 4-NP under visible light irradiation is weaker than H_2O_2 .

3.6.2. Influence of H_2O_2 concentration on the rate of degradation

The degradation efficiency versus different initial concentrations of H_2O_2 has been summarized in Fig. 8. The photodegradation efficiency increased with an increase of H_2O_2 concentration up to 0.12 mol/L and then decreased slowly, which suggested that an optimum concentration of H_2O_2 could be 0.12 mol/L.

At low concentrations of H_2O_2 , the hydroxyl radicals increased when increasing the concentrations of H_2O_2 , so the efficiency of 4-NP degradation enhanced correspondingly. However, excess H_2O_2 in the suspensions could cause the consumption of hydroxyl radicals, because H_2O_2 can react with hydroxyl radicals to form a weak oxidant HO_2^{\bullet} (Eq. (R1)), and at the same time, hydroxyl radicals can also dimerize to H_2O_2 at high concentration (Eq. (R2)) [23,24].

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2 {}^{\bullet} + H_2O \tag{R1}$$

$${}^{\bullet}\text{OH} + {}^{\bullet}\text{OH} \rightarrow H_2\text{O}_2 \tag{R2}$$

3.6.3. Photocatalytic mechanism and the role of H_2O_2

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A possible photocatalytic mechanism involving H_2O_2 was proposed based on the reported mechanism both under UV and visible light irradiation by using modified TiO₂ photocatalyst [25–27], as shown in Eqs. (1)–(7) and Fig. 9.

$$CuPp-TiO_2 \xrightarrow{h\nu > 400 \text{ nm}} [CuPp^+ - TiO_2(e^-)]^*$$
(1)

$$[CuPp^{+}-TiO_{2}(e^{-})]^{*} + H_{2}O_{2} \rightarrow [CuPp^{+}-TiO_{2}] + {}^{\bullet}OH + OH^{-}$$
(2)

$$[CuPp^+-TiO_2(e^-)]^* + O_2 \rightarrow [CuPp^+-TiO_2] + O_2^{\bullet}$$
 (3)

 $^{\bullet}$ OH + 4-NP \rightarrow Oxidatiion products

 $O_2^{\bullet-} + 4 \text{-NP} \rightarrow \text{Oxidatiion products}$ (5)

$$O_2^{\bullet-} + H_2O_2 \to {}^{\bullet}OH + OH^- + O_2$$
 (6)

$$[CuPp^+-TiO_2] + 4-NP \rightarrow CuPp-TiO_2 + oxidation products$$
(7)

CuPp-TiO₂
$$\xrightarrow{m^{2} + 400\text{ mm}}$$
 [CuPp⁺-TiO₂(e^{*})]^{*} (1)
[CuPp⁺-TiO₂(e^{*})]^{*} + H₂O₂ \longrightarrow [CuPp⁺-TiO₂] + \cdot OH + OH⁻ (2)
[CuPp⁺-TiO₂(e^{*})]^{*} + O₂ \longrightarrow [CuPp⁺-TiO₂] + O₂⁻ (3)
 \cdot OH + 4-NP \longrightarrow Oxidation Products (4)
O₂⁻⁻ + 4-NP \longrightarrow Oxidation Products (5)
O₂⁻⁻ + H₂O₂ \longrightarrow \cdot OH + OH⁻ + O₂ (6)
[CuPp⁺-TiO₂] + 4-NP \longrightarrow CuPp-TiO₂ + Oxidation Products (7)
 $\xrightarrow{O_{2}}$ $\xrightarrow{H_{2}O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{H_{2}O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{H_{2}O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{H_{2}O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}}$ $\xrightarrow{O_{2}$ $\xrightarrow{O_{2}$

Fig. 9. The diagram of photocatalytic mechanism.

H₂O₂

E vs NHE

Under the visible light irradiation, the process of CuPp–TiO₂ photocatalytic reaction can be intrigued by the excitation of the ground state of the sensitizer CuPp via one photon transition ($h\nu$) to its excited state [CuPp⁺–TiO₂(e⁻)]^{*} (Eq. (1)), then the photo-induced electrons inject into the conduction band (CB) of TiO₂, and finally the reactive electrons can be trapped by adsorbed H₂O₂ or O₂ on the surface of TiO₂ and produce reactive species •OH and O₂•⁻ (Eqs. (2) and (3)). The •OH from H₂O₂ can photodegrade the 4-NP efficiently (Eq. (4)), but O₂•⁻ is less reactive with 4-NP in the absence of H₂O₂ and the reaction of Eq. (5) can happen to a small extent. In the presence of H₂O₂, the O₂•⁻ can react with H₂O₂ and produce hydroxyl radicals quickly (Eq. (6)), and finally, degrade the 4-NP effectively. [CuPp⁺–TiO₂] can be reduced by 4-NP to its ground state (Eq. (7)) [28,29].

The role of H_2O_2 can be clearly seen from the analysis of the photocatalytic mechanism. Firstly, the H_2O_2 reacts directly with the photo-induced electrons to produce hydroxyl radicals (Eq. (2)) in the presence of CuPp–TiO₂ photocatalyst, and secondly, more hydroxyl radicals can be produced by the reaction of $O_2^{\bullet-}$ and H_2O_2 (Eq. (6)). In a word, the visible-light-driven photocatalytic efficiency of CuPp–TiO₂ can be improved greatly by adding an appropriate amount of H_2O_2 .

4. Conclusions

(4)

The photocatalytic activity of a new CuPp–TiO₂ photocatalyst has been studied by carrying out the photodegradation of 4-NP in the presence of H₂O₂ under visible light irradiation firstly. It has been found that anion superoxide (O₂•⁻) is mainly formed in the absence of H₂O₂ and O₂•⁻ itself is less active for the degradation of 4-NP, so the photocatalytic activity of CuPp–TiO₂ is low under visible irradiation. However, by adding an appropriate amount of H₂O₂, the visible-light-driven photocatalytic efficiency of CuPp–TiO₂ is enhanced greatly, because the H₂O₂ can react with O₂•⁻ in water and produce hydroxyl radicals quickly, and finally the hydroxyl radicals degrade the 4-NP into small molecules.

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References

- [1] A.L. Linsebigler, G. Lu, J.T. Yates, Chem. Rev. 95 (1995) 735-758.
- [2] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69-96.
- [3] J. Ananpattarachai, P. Kajitvichyanukul, S. Seraphin, J. Hazard. Mater. 168 (2009) 253–261.
- [4] G. Mele, R.D. Sole, G. Vasapollo, E.G. López, L. Palmisano, M. Schiavello, J. Catal. 217 (2003) 334–342.
- [5] J. Li, Suyoulema, W. Wang, Sarina, Solid State Sci. 11 (2009) 2037-2043.
- [6] Q. Xiao, L.L. Ouyang, J. Phys. Chem. Solids 72 (2011) 39-44.
- [7] F.Y. Shen, W.X. Que, Y.L. Liao, X.T. Yin, Ind. Eng. Chem. Res. 50 (2011) 9131–9137.
- [8] A.V. Rupa, D. Manikandan, D. Divakar, T. Sivakumar, J. Hazard. Mater. 147 (2007) 906–913.
- [9] J. Wang, J. Li, Y.P. Xie, C.W. Li, G.X. Han, L.Q. Zhang, R. Xu, X.D. Zhang, J. Environ. Manage. 91 (2010) 677–684.
- [10] S. Chu, X. Zheng, F. Kong, G. Wu, L. Luo, Y. Guo, H. Liu, Y. Wang, H. Yu, Z. Zou, Mater. Chem. Phys. 129 (2011) 1184–1188.
- [11] D.M. Chen, D. Yang, J.Q. Geng, J.H. Zhu, Z.Y. Jiang, Appl. Surf. Sci. 255 (2008) 2879–2884.
- [12] H.Y. Huang, X.T. Gu, J.H. Zhou, K. Ji, H.L. Liu, Y.Y. Feng, Catal. Commun. 11 (2009) 58–61.

- [13] G. Mele, R.D. Sole, G. Vasapollo, E.G. Lòpez, L. Palmisano, Green Chem. 6 (2004) 604–608.
- [14] P. Moro, M.P. Donzello, C. Ercolani, F. Monacelli, G. Moretti, J. Photochem. Photobiol. A 220 (2011) 77–83.
- [15] G. Mele, R.D. Sole, G. Vasapollo, J. Phys. Chem. B 109 (2005) 12347-12352.
- [16] X.S. Feng, S.Z. Kang, H.G. Liu, J. Mu, Thin Solid Films 352 (1999) 223-227.
- [17] X.F. Lü, J. Li, C. Wang, M.Y. Duan, Y. Luo, G.P. Yao, J.L. Wang, Appl. Surf. Sci. 257 (2010) 795-801.
- [18] C. Wang, G.M. Yang, J. Li, G. Mele, R. S1ota, M.A. Broda, M.Y. Duan, G. Vasapollo, X.F. Zhang, F.X. Zhang, Dyes Pigments 80 (2009) 321–328.
- [19] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, J. Org. Chem. 32 (1967) 476.
- [20] M.Y. Duan, J. Li, G. Mele, C. Wang, X.F. Lü, G. Vasapollo, F.X. Zhang, J. Phys. Chem. C 114 (2010) 7857–7862.
- [21] J.C. Tristao, F. Magalhaes, P. Corio, M.T.C. Sansiviero, J. Photochem. Photobiol. A 181 (2006) 152-157.
- [22] C.E. Diaz-Uribe, M.C. Daza, F. Martínez, E.A. Páez-Mozob, C.L.B. Guedes, E.D. Mauro, J. Photochem. Photobiol. A 215 (2010) 172–178.
- [23] G.G. Oliveros, E.A. Páez-Mozo, F.M. Ortega, Appl. Catal. B: Environ. 89 (2009) 448-454.
- [24] N. Daneshvar, M.A. Behnajady, Y.Z. Asghar, J. Hazard. Mater. 139 (2007) 275-279.
- [25] C. Wang, J. Li, G. Mele, G.M. Yang, F.X. Zhang, L. Palmisano, G. Vasapollo, Appl. Catal. B: Environ. 76 (2007) 218-226.
- [26] H.Y. Huang, X.T. Gu, J.H. Zhou, Catal. Commun. 11 (2009) 58-61.
- [27] D. Chatterjee, S. Dasgupta, J. Photochem. Photobiol. C 6 (2005) 186-205.
- [28] X.Z. Li, C.C. Chen, J.C. Zhao, Langmuir 17 (2001) 4118-4122.
- [29] Y.F. Rao, W. Chu, Environ. Sci. Technol. 43 (2009) 6183-6189.