Preparation, characterization and photocatalytic activity of metalloporphyrins-modified TiO₂ composites

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Abstract Three new Cu(II), Zn(II), Co(II) 5,15-di (4-hydroxyphenyl)-10, 20-diphenyl-porphyrin (CuDHPP, ZnDHPP, CoDHPP) and the corresponding metalloporphyrins–TiO₂ photocatalysts CuDHPP–TiO₂, ZnDHPP–TiO₂, CoD-HPP–TiO₂ were synthesized and characterized by SEM, XRD, FT-IR, and DRS. The results revealed that the metalloporphyrins impregnated onto the surface of TiO₂ did not change the phase composition and particle sizes of TiO₂ samples, but increased the photocatalytic efficiency. In addition, photoluminescence study showed that the three photocatalysts could successfully increase the separation efficiency of the photoinduced electron and hole. The photodegrading 4-NP experiments indicated that the three photocatalysts greatly enhanced the photocatalytic activity of bare TiO₂, and the photocatalytic activity of CuDHPP–TiO₂ was the highest. Moreover, the possible mechanism for the photodegradation of 4-NP was also proposed.

Keywords Metalloporphyrins \cdot TiO₂ \cdot Photocatalytic degradation \cdot 4-Nitrophenol \cdot Mechanism

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Introduction

In recent years, there has been growing concern over many serious environmental problems. It is, therefore, of the utmost urgency to develop ecologically clean and safe chemical technologies, materials, and/or processes to sustain our present level of population and economic expansion [1, 2]. 4-Nitrophenol as an important organic intermediate is widely used in the production of pesticides, insecticides, herbicides, and synthetic dyes, but their toxic effects on human health are well documented [3, 4]. As we all know, photocatalysis is a promising low-cost alternative method for the treatment and purification of contaminated water compared with other technologies [5, 6]. TiO₂ is believed to be one of the most active photocatalysts. However, a critical drawback of TiO_2 is the large band gap (3.2 eV), which is too large to absorb solar energy effectively. In addition, the high degree of recombination between photoinduced electrons and holes also blocks its practical application [7–9]. So a lot of effort has been devoted to studying how to extend its light response [10-12]. Among them, the metalloporphyrin-modified TiO_2 system has been proposed for the photocatalytic degradation of various kinds of organic pollutants in water, as porphyrin compounds possess good chromophore activities over the solar spectrum and good electrondonating properties due to their large π -electron systems [13–15].

Metalloporphyrins with different functional groups (–COOH, –OH, etc.) in the periphery of the porphyrin ring have been employed as photosensitizers for pollutant photodegradation [16–18]. It has been found that these functional groups can interact with the surface of TiO_2 and, consequently, display different photocatalytic activity in degrading pollutants.

Motivated by the above work, we here report a novel functionalized porphyrin 5, 15-di (4-hydroxyphenyl)-10, 20-diphenyl-porphyrin (H₂DHPP) and their corresponding metalloporphyrins MDHPP (M=Co(II), Cu(II), Zn(II)) (Fig. 1). The MDHPP–TiO₂ photocatalysts were then synthesized and characterized by SEM, XRD, FT–IR, and DRS. The further photocatalytic activities of the MDHPP–TiO₂ samples were evaluated in the photocatalytic degradation of 4-nitrophenol in aqueous solution under the halogen lamp irradiation. The PL spectra of the three photocatalysts showed that they could successfully improved charge separation than bare TiO₂, which leads to a higher photocatalytic activity. Furthermore, a possible mechanism of the photodegradation of 4-NP was also proposed.

Fig. 1 The structure of porphyrin and their metalloporphyrins



Materials

P-Hydroxybenzaldehyde, benzaldehyde, pyrrole, and dichloromethane were obtained from Tianjin Chemical Reagents, China. All these chemicals were used without further purification except pyrrole, which was distilled before use. The commercial TiO₂ was purchased from Acros Organics, USA (Anatase phase). The target pollutant 4-nitrophenol (4-NP) was obtained from Xi'an Chemical, China. Distilled water was used throughout the 4-NP removal experiments.

Characterizations

The scanning electron microscopy (SEM; Hitachi-S4800) was used to characterize the morphologies of the samples. Diffuse reflectance UV–vis spectra were recorded on a Shimadzu UV-3100 spectrophotometer with BaSO₄ as reference. The FT-IR spectra were recorded on a BEQUZNDX-550 FT-IR spectrometer using KBr pellets in the range 4,000–400 cm⁻¹. The X-ray diffraction (XRD) measurement was performed with a Bruker D8 diffractometer using graphite monochromatic copper radiation (Cu K α) at 40 kV, 30 mA over the 2 θ range 20–80°. Photoluminescence spectra (PL) were measured at room temperature on a Hitachi FL-4500 fluorescence spectrometer using a Xe lamp with an excitation wavelength of 330 nm.

Synthesis of porphyrin (H₂DHPP) and metalloporphyrins (MDHPP)

5, 15-di (4-hydroxyphenyl)-10, 20-diphenyl-porphyrin (H_2DHPP) was synthesized according to the methods described in the literature [18].

P-Hydroxybenzaldehyde (30 mmol, 3.66 g) and benzaldehyde (30 mmol, 3.07 mL) were added to 150 mL propionic acid. Then, pyrrole (60 mmol, 4.15 mL) was added dropwise and the resulting mixture was vigorous stirred at 145 °C for 50 min. After cooling and the solvent removal under vacuum, the residue was dissolved in CH₂Cl₂ and purified on silica-gel with dichloromethane/ hexane as eluant. A desired purple-black solid of H₂DHPP was successfully obtained. Yield: 38 %. Mp: >250 °C, Anal. Calcd. for C₄₄H₃₀N₄O₂ (Mol. wt: 646.24), %: C, 81.73 (81.71); H, 4.62 (4.68); N, 8.69 (8.66). MS: *m/z* 647.53([M + H]⁺) amu. UV–vis (CH₂Cl₂): λ_{max}/nm , 418 (Soret band), 479, 515, 549, 592 (Q bands). FT-IR: v, cm⁻¹, 3,341, 2,963, 2,923, 2,361, 1,576, 1,418, 1,261, 1,096, 1,023, 964, 801, 697.

Copper, zinc, and cobalt porphyrins were synthesized by treating H₂DHPP (0.33 mmol) with an excess of Cu(OAc)₂·H₂O, Zn(OAc)₂·2H₂O or Co(OAc)₂·4H₂O in CH₂Cl₂ (30 mL) for 12 h at room temperature, respectively. The mixture was monitored by TLC until the complete disappearance of the starting material H₂DHPP. The unreacted acetic acid salt was filtrate and the solvent removed under vacuum. The crude product was purified by chromatography on a silica-gel column with CH₂Cl₂ as eluant. Metalloporphyrins (CuDHPP, ZnDHPP, CoDHPP) were obtained in nearly quantitative yields.

CuDHPP

Yield: 95 %. Mp: >250 °C, Anal. Calcd. for $C_{44}H_{28}N_4O_2Cu$ (Mol. wt: 707.15), %: C, 74.59 (74.61); H, 4.03 (3.98); N, 7.89 (7.91). MS: *m/z* 708.02 ([M + H]⁺) amu. UV–vis (CH₂Cl₂): λ_{max} /nm, 418 (Soret band), 539, 575 (Q bands). FT-IR: v, cm⁻¹, 3,423, 2,923, 2,852, 1,659, 1,606, 1,510, 1,436, 1,384, 1,343, 1,263, 1,168, 1,099, 1,068, 999, 797, 702.

ZnDHPP

Yield: 95 %. Mp: >250 °C, Anal. Calcd. for $C_{44}H_{28}N_4O_2Zn$ (Mol. wt: 708.15), %: C, 74.39 (74.42); H, 3.98 (3.97); N, 7.91 (7.89). MS: *m/z* 709.33 ([M + H]⁺) amu. UV–vis (CH₂Cl₂): λ_{max} /nm, 421 (Soret band), 560, 600 (Q bands). FT-IR: v, cm⁻¹, 3,424, 2,923, 1,709, 1,657, 1,607, 1,550, 1,485, 1,436, 1,384, 1,336, 1,263, 1,168, 1,099, 1,066, 997, 796, 701, 668, 583.

CoDHPP

Yield: 93 %. Mp: >250 °C, Anal. Calcd. for $C_{44}H_{28}N_4O_2Co$ (Mol. wt: 709.15),%: C, 75.09 (75.10); H, 4.05 (4.01); N, 8.01 (7.96). MS: *m/z* 710.43 ([M + H]⁺) amu. UV–vis (CH₂Cl₂): λ_{max} /nm, 418 (Soret band), 548, 587 (Q bands). FT-IR: v, cm⁻¹, 3,427, 2,925, 2,361, 1,615, 1,551, 1,453, 1,385, 1,263, 1,169, 1,056, 874, 802, 669, 615.

Preparation of MDHPP-TiO₂ photocatalysts

MDHPP–TiO₂ photocatalysts used as photocatalysts for the photodegradation experiments were prepared in the following way: 6 μ mol amounts of CuDHPP, ZnDHPP, or CoDHPP were dissolved in 30 mL of CH₂Cl₂, respectively, and then 1 g of finely ground TiO₂ was added to this solution. The resulting suspension was magnetically stirred at room temperature for 12 h. Then, the solvent was removed under vacuum and the photocatalyst was collected. Afterwards, the surface of white TiO₂ displayed the corresponding color of the photocatalyst, which demonstrated that the MDHPP had been impregnated onto the surface of TiO₂ nanoparticles.

Evaluation of photocatalytic activity

Photocatalytic activities of MDHPP–TiO₂ composites were evaluated for the photodegradation of 4-NP using a Model XPA-VII photocatalytic reactor (Xujiang Electromechanical Plant, Nanjing, China). A 400-W halogen lamp with wavelength emissions closely mimicking solar radiation was served as the light source [19]. The distance between the light source and the reactor was 12 cm and the light intensity was 615 mw cm⁻². The system was cooled by circular water running via an interlayer and magnetic agitation was used so that the photocatalysts can be suspended in the solution.

In a typical experiment, 4-NP (50 mL, 1×10^{-4} mol/L) and 10 mg of the photocatalysts were placed in the quartz socket tube. Before irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure the establishment of adsorption equilibrium between the photocatalysts and 4-NP. At a given time interval, about 3 mL of the suspension was withdrawn, and the photocatalysts were separated from the suspensions by filtration. The photodegradation process was monitored by its characteristic absorption band of 4-NP at 317 nm using a UV-vis spectrophotometer (UV-1800; Shimadzu). Based on the correlation between concentration and absorption, $C/C_0 = A/A_0$, the decomposition efficiency was calculated.

Results and discussion

Morphology of photocatalysts

SEM observation can reveal that the samples consisted of aggregates of particles. Figure 2 shows the representative micrographs obtained for the bare TiO_2 before and after being treated with CuDHPP, ZnDHPP, and CoDHPP, respectively. It can be observed that the microsphere possesses a similar surface condition, indicating that the TiO₂ microsphere basically were no change before and after impregnated with the metalloporphyrins.



Fig. 2 SEM images of bare TiO_2 (a), $CuDHPP-TiO_2$ (b), $ZnDHPP-TiO_2$ (c), and $CoDHPP-TiO_2$ (d) photocatalysts

XRD characterization of photocatalysts

In order to confirm the crystal identity of TiO_2 samples and the effect of MDHPP on the crystal structure of TiO_2 , XRD spectra were recorded. As shown in Fig. 3, all the characteristic peaks are well matched with that of anatase TiO_2 (JCPDS file no. 12–1272). When MDHPP is impregnated onto the surface of TiO_2 , no detectable other peaks are observed for the MDHPP– TiO_2 photocatalysts, speculating that the content of MDHPP are small and/or well dispersed on the surface of TiO_2 , which suggests that the MDHPP impregnated onto the surface of TiO_2 does not change the bulk intrinsic property of the TiO_2 photocatalyst [20].

FT-IR spectra of photocatalysts

To further investigate the interaction between MDHPP molecules and TiO₂ nanoparticles, the FT-IR spectra of bare TiO₂, CuDHPP–TiO₂, ZnDHPP–TiO₂, and CoDHPP–TiO₂ were measured. As shown in Fig. 4, for bare TiO₂, the vibrations at 3,425 and 1,631 cm⁻¹ observed correspond to the stretching vibrations and the bending vibration of –OH on the surface of TiO₂, respectively. It indicates that there exist large amounts of hydroxy groups, which is helpful for anchoring MDHPP molecules on the surface of TiO₂ by the interaction of hydroxyl groups [21]. Furthermore, when MDHPP is impregnated onto the surface of bare TiO₂, the main characteristic vibrations attributed to the C–C at ~1,400 cm⁻¹ and C–H ~2,920 cm⁻¹ at of MDHPP can be clearly observed, which indicate that the TiO₂ modified by MDHPP has been successfully achieved.

UV-visible diffuse reflectance spectra of photocatalysts

The optical property of a semiconductor is one of the important factors determining its photocatalytic performance [22]. As shown in Fig. 5, the UV–visible diffuse reflectance spectra of the bare TiO_2 and MDHPP– TiO_2 photocatalysts were recorded in the range of 300–700 nm. It is obvious that there was no absorption





above 400 nm for the bare TiO_2 , whereas the MDHPP– TiO_2 photocatalysts exhibit the feature peaks of MDHPP observed in CH_2Cl_2 solution (Table 1), which indicated that MDHPP successfully loaded onto the TiO_2 surface with integrated metalloporphyrin framework, and led to broader absorption range for bare TiO_2 . It was noticed that the Soret and Q bands of the MDHPP– TiO_2 are all shifted and broadened relatively to MDHPP observed in CH_2Cl_2 solution, implying that there exist a weak interaction between TiO_2 and metalloporphyrins molecules.

Photoluminescence (PL) spectra of photocatalysts

Photoluminescence (PL) emission spectra have been widely used to investigate the efficiency of charge carrier trapping, immigration and transfer and to understand the fate of electron-hole pairs in semiconductor particles [23]. As can be observed in Fig. 6, three peaks around 400, 465, and 525 nm are observed for the bare TiO₂. Generally, the peak at 400 nm can be attributed to self-trapped excitation localized in the TiO₆ octahedron, and the peak at 465 nm to oxygen vacancies. Peak at



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Compounds	MDHPP		MDHPP-TiO ₂	
	Soret band $\lambda \max(nm)$	Q bands $\lambda \max(nm)$	Soret band $\lambda \max(nm)$	Q bands $\lambda \max(nm)$
CuDHPP	418	539, 575	415	542, 592
ZnDHPP	420	560, 600	425	562, 604
CoDHPP	418	548, 587	430	556, 595

Table 1 UV-visible spectra data of the MDHPP in CH_2Cl_2 and UV-visible diffuse reflectance spectra data of MDHPP-TiO₂ photocatalysts

525 nm is assigned to the oxygen vacancy with one trapped electron [24–26]. The spectra of the three photocatalysts showed similar curve shape except for the peak intensities. The bare TiO_2 sample showed the highest PL emission intensity, indicating that electrons and holes were more easily recombined. However, the PL emission intensity decreased greatly in the three photocatalysts. So it indicated that the MDHPP–TiO₂ have lower recombination of electrons and holes. Furthermore, it can be deduced that the photo-produced electrons of the excited CuDHPP–TiO₂ molecules may easily transfer effectively to the conduction band (CB) of the TiO_2 than ZnDHPP and CoDHPP, which reasonably leads to a higher photocatalytic activity since the photodegradation reactions are evoked by these charge carriers [17].

Photocatalytic activity and photocatalytic mechanism

The photocatalytic activity for the degradation of 4-NP in aqueous suspension under the halogen lamp irradiation using MDHPP–TiO₂ and CuTPP–TiO₂ (as for comparison) were tested. Obviously, as shown in Fig. 7, the blank experiment showed that the 4-NP was hardly photodegraded in the absence of any photocatalyst. After 60 min of irradiation, the three new photocatalysts, CuDHPP–TiO₂, ZnDHPP– TiO₂, and CoDHPP–TiO₂, showed much enhanced photoactivity compared with bare TiO₂, and in particular CuDHPP–TiO₂ exhibited the highest efficiency of all samples,



as the following order and their corresponding photodegradation efficiency in parentheses:

 $\label{eq:cudHPP-TiO2} \begin{array}{l} (95.8 \ \%) > ZnDHPP-TiO_2 \ (85.6 \ \%) > CoDHPP-TiO_2 \ (80. \\ 8 \ \%) > CuTPP-TiO_2 \ (66.8 \ \%) > bare \ TiO_2. \end{array}$

These results indicated that metal ion plays an important role in the photoreactivity. Meanwhile, the anchoring group (–OH) of metalloporphyrin on the TiO_2 is also a main factor for the photodegradation efficiency. In addition, the photoelectrons can be transferred more efficiently from the excited MDHPP molecules to the conduction band of TiO_2 [27, 28], which improve the separation of photogenerated electrons and holes, resulting in the photodegradation of 4-NP finally. Furthermore, the photocatalyst of CuDHPP– TiO_2 shows the best photocatalytic activity due to its sharply inhibiting of the electrons and holes of combination, which could be attributed to the lowest PL emission intensity of the three photocatalysts.

Based on the above experimental results, we propose a mechanism accounting for the photocatalytic degradation of 4-NP over MDHPP–TiO₂ and bare TiO₂ under halogen lamp irradiation. It is demonstrated in Fig. 8. On the one hand, TiO₂ itself can be excited to create mobile electrons and then the photoinduced electrons inject into the CB of TiO₂ (Eq. 1). Thus, the holes, created in the VB of TiO₂, can also immigrate faster to the 4-NP molecules through the MDHPP, which has the potential to photodegrade 4-NP into small molecules or CO₂, H₂O (Eq. 2) [29]. On the other hand, the excitation of ground state of the [MDHPP] can be excited to its excited state [MDHPP]*, and the excited state electrons could readily inject into the CB of TiO₂ (Eq. 3). The excited electrons in the CB of TiO₂ reacted with absorbed O₂, and then O₂⁻⁻ or •OH were subsequently formed, which will oxidize 4-NP into small molecules or CO₂, H₂O (Eqs. 4–6) [30]. In addition, according to the previous work [31, 32], [MDHPP]⁺ can be reduced by 4-NP to its ground state (Eq. 7).

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$$\text{TiO}_2 \xrightarrow{OV} \text{TiO}_2(e^-) + \text{TiO}_2(h^+)$$
 (1)

Fig. 7 Photocatalytic activity of 4-NP as a function of irradiation time over under halogen lamp irradiation using different photocatalysts





$$\text{TiO}_2(h^+) \xrightarrow{h^+ \text{transfer}} \text{MDHPP}(h^+) \xrightarrow{4-\text{NP}} \text{CO}_2, \text{ H}_2\text{O}, \text{ and other small molecules}$$
 (2)

$$\mathrm{TiO}_{2}[\mathrm{MDHPP}] \xrightarrow{\nu_{13}} \mathrm{TiO}_{2}[\mathrm{MDHPP}]^{*} \rightarrow [\mathrm{MDHPP}]^{+} + \mathrm{TiO}_{2}(\mathrm{e}^{-})$$
(3)

$$\mathrm{TiO}_{2}(\mathrm{e}^{-}) + \mathrm{O}_{2} \to \mathrm{TiO}_{2} + \mathrm{O}_{2}^{\cdot-} \tag{4}$$

$$O_2^{-} + H_2 O \rightarrow \cdots \rightarrow \cdot OH + OH^-$$
 (5)

$$O_2^{-}$$
 or $\cdot OH + 4 - NP \rightarrow CO_2 + H_2O$ and other small molecules (6)

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

Conclusions

In this work, three new metalloporphyrins MDHPP [M=Cu(II), Co(II), and Zn(II)]modified TiO₂ composites have been synthesized and characterized. The SEM, XRD, DRS, and FT-IR spectra demonstrated that MDHPP were successfully impregnated onto the surface of TiO₂ microsphere and did not influence the morphology of TiO₂. Furthermore, the three photocatalysts of MDHPP–TiO₂ have lower recombination of electrons and holes than bare TiO₂ from the PL spectra. The photocatalytic activity experiment indicated that the three photocatalysts greatly enhanced the photocatalytic efficiency of bare TiO₂ in photodegrading the 4-NP, and CuDHPP–TiO₂ shows the best photocatalytic activity. This can be explained by the synergic effect between the metal ion and the –OH group improved the separation of photogenerated electrons and holes, which reasonably leads to a higher photocatalytic activity than bare TiO₂. Furthermore, a possible photocatalytic mechanism has also been discussed.

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