



Thermally-assisted photodegradation of lignin by TiO₂/H₂O₂ under visible/near-infrared light irradiation

Jun Chen¹, Wenxia Liu^{1*}, Zhenzhen Li¹ and Hong Liu²

ABSTRACT As a bio-recalcitrant organic pollutant in paper mill effluent, lignin is generally removed by an advanced oxidation process, such as a TiO₂/H₂O₂ photocatalytic technique under irradiation with ultraviolet light, which only accounts for less than 5% of sunlight. Herein, we reported a TiO₂/H₂O₂-based thermally-assisted photocatalytic process that allows lignin to be efficiently degraded under visible/near-infrared light at an elevated temperature. Adsorption of H₂O₂ on TiO₂ nanoparticles and an increase of temperature facilitate the production and separation of charge carriers under near-infrared and visible light irradiation, accelerate carrier transfer at the TiO₂-electrolyte interface and promote the production of hydroxyl radicals. A higher level of H₂O₂ addition results in an increased degradation rate of lignin, while the optimal temperature for the thermally-assisted photodegradation of lignin is 70°C. A charge carrier excitation and transfer process was proposed for the TiO₂/H₂O₂ thermally-assisted photocatalytic process. This work describes a new method for the photodegradation of organic pollutants, such as residual lignin in paper mill effluent, using wide band gap semiconductors under visible and near-infrared light irradiation.

Keywords: lignin, thermally-assisted photocatalysis, TiO₂, H₂O₂, near-infrared light

INTRODUCTION

Lignin is an aromatic biopolymer separated from cellulose materials in the pulping process. It is one of the major components of wastewater from pulp and paper mills, causing the dark brown coloration and environmental pollution of pulp and paper effluents [1]. Lignin is generally difficult to be effectively removed in conventional treatment processes because of its high resistance to microbial degradation [2,3]. A combination of conventional biological treatment with advanced oxidation

processes (AOPs) to remove the bio-recalcitrant lignin derivatives has become a promising strategy in the treatment of pulp and paper mill effluents [4,5].

As a post-treatment of the biological process, AOPs generally decontaminate waters by *in situ* generating very reactive free radicals, such as hydroxyl radicals, at sufficient concentrations to completely mineralize and eliminate organic constituents without harmful environmental impact [4–6]. The hydroxyl radicals may be produced by means of various chemical, photochemical, sonochemical or electrochemical reactions [6]. Among these methods, the photochemical processes, especially heterogeneous photocatalytic process involving semiconductors and ultraviolet (UV) irradiation, such as TiO₂/UV, Fe₂O₃-TiO₂/UV, ZnO/UV, ZnO/O₂/UV and TiO₂/H₂O₂/UV, have attracted significant attention in the degradation of lignin [7–10]. Wide band gap semiconductors, such as TiO₂ and ZnO, are employed due to their high valence band potentials. TiO₂ and ZnO generally photogenerate holes with potentials higher than the redox potential of H₂O/·OH, favoring the production of hydroxyl radicals. The introduction of H₂O₂ or O₂ in photocatalytic processes generally further improves the photocatalytic performance of TiO₂ or ZnO by either trapping photogenerated electrons to suppress the recombination of photogenerated electrons and holes or by accepting electrons to produce additional hydroxyl radicals [10,11]. Because semiconductors can only be excited by light with energy greater than their band gaps, UV light has to be used as the excitation source for TiO₂ and ZnO with band gaps wider than 3.0 eV.

Fully using solar energy is one of the driving forces to develop photocatalytic processes for the degradation of organic pollutants. UV light accounts for less than 5% of sunlight. Therefore, the visible and near-infrared (NIR) radiation that account for more than 90% of sunlight have

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not been efficiently used in conventional heterogeneous photocatalytic mineralization of pulp and paper mill effluents. Developing visible and NIR active photocatalytic processes is key for the full use of solar energy in the photodegradation of organic pollutants [12–14]. Many strategies for extending the photocatalytic activity of TiO₂ and ZnO to the visible light region have been developed in paper mill effluent treatments, such as loading narrow band gap semiconductors [15], noble metals [16], or dye-sensitization [17]. However, these strategies only extend the photocatalytic performance of UV active TiO₂ and ZnO to the visible light region.

In this study, a new strategy, i.e., thermal treatment, for extending the photocatalytic activity of TiO₂/H₂O₂ to the visible and NIR region was put forward for the photodegradation of lignin. The thermal treatment induced the production and separation of photogenerated carriers, significantly reduced the charge transfer resistance and promoted the production of hydroxyl radicals on TiO₂ nanoparticle surfaces under NIR and visible light irradiation. Consequently, the TiO₂/H₂O₂ thermally-assisted photocatalytic system was found to be highly efficient for the photodegradation of lignin-containing effluent under the irradiation of near-infrared lamp and solar light. This TiO₂/H₂O₂ based photocatalytic process is a new method for the photo-treatment of paper mill effluent under solar light irradiation.

EXPERIMENTAL SECTION

Materials

TiO₂ (P25, ca. 80% anatase and 20% rutile), a white powder with an average primary particle size of 21 nm and a specific surface area of $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$, was a commercial product of Evonik Degussa GmbH. Alkali lignin (CAS 8068-05-1) was purchased from Shanghai Yuanye Bio-Technology Co., Ltd (China). Hydrogen peroxide (H₂O₂, 30% w/v), hydrochloric acid (HCl, 37.5% w/v), sodium hydroxide (NaOH), and sodium sulfate (Na₂SO₄) were purchased from Sinopharm Chemical Reagents Co., Ltd (Shanghai, China). All the chemicals were used as received without further purification. Deionized water was used throughout this study.

Thermally-assisted photodegradation of lignin

The thermally-assisted photodegradation of lignin under irradiation with an infrared lamp was carried out in an assembled experimental device (Fig. S1, Supplementary information), where a 200 W near-infrared lamp was employed as the light source and a water bath was used to control the temperature. The NIR lamp emitted a minor

portion of visible light and a major portion of NIR light (Fig. S2). In a typical experiment, 20 mg of TiO₂ powder was suspended in 20 mL of 50 mg L⁻¹ lignin aqueous solution followed by the addition of 0–20 μL hydrogen peroxide in a 50-mL Teflon container. After sonication for several minutes, the container was then transferred to the water-bath pre-heated to 70°C and irradiated under the near-infrared lamp. At given time intervals, 4 mL aliquots of the suspension were collected and immediately centrifuged at 10,000 rpm for 5 min to remove the TiO₂. The UV-vis absorption spectra of the residual lignin were collected on an Agilent 8453 UV-vis spectrophotometer. The degradation rate of lignin was calculated based on the variation of absorbance at 205 nm before and after lignin degradation.

Characterization

X-ray powder diffraction (XRD) patterns of TiO₂ samples before and after thermally-assisted photodegradation of lignin were recorded on a Bruker D8 Advance powder X-ray diffractometer with Cu Kα radiation ($\lambda=0.15406 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) was used to detect the variation of surface elemental compositions and valance states of the TiO₂ sample after the adsorption of hydrogen peroxide or the thermally-assisted photodegradation of lignin. All of the binding energies were calibrated by the C 1s peak at 284.8 eV. The zeta potentials of the TiO₂ samples were determined by a Zetasizer 3000 HSA (Malvern Instruments, UK). Photoelectrochemical measurements were performed on a CHI660E electrochemical workstation (Chenhua Ins., Inc., Shanghai, China) with a standard three-electrode assembly using Ag/AgCl as the reference electrode, Pt wire as the counter electrode and TiO₂-coated fluorine-doped tin oxide (FTO) conductive glass as the working electrode [13,18]. The electrolyte was 0.5 mol L⁻¹ Na₂SO₄ solution (pH 6.8). A 300 W Xe arc lamp (CEL-HXUV 300) with a cut-off filter either below 800 nm or below 420 nm was used as the NIR or visible light sources, respectively. Electron spin resonance (ESR) spectroscopy was used to investigate hydroxyl radical generation of the TiO₂/H₂O₂ thermally-assisted photocatalytic system under visible light irradiation, and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was used for the spin trap. ESR spectra were recorded on a Bruker E500 spectrometer.

RESULTS AND DISCUSSION

Thermally-assisted photocatalytic activity and degradation on lignin

The activity of TiO₂/H₂O₂ thermally-assisted photo-

catalytic system was evaluated by the degradation of methyl orange (MO), a stable azo dye generally used as a model organic pollutant [13,19]. The results show that the concentration of MO was hardly changed when the MO was irradiated for 3 h under the infrared lamp at ambient temperature (Fig. S3) due to the wide band gap of TiO_2 . However, when the sample was heated to 75°C , nearly 50% of the MO was removed, even in dark conditions, while nearly 90% of the MO was removed under irradiation with the infrared lamp within 3 h, suggesting that both temperature and light irradiation play key roles in the thermally-assisted photocatalytic degradation of MO in the presence of $\text{TiO}_2/\text{H}_2\text{O}_2$. The elevated temperature may provide additional energy for photogenerating carriers on the TiO_2 surfaces under infrared lamp irradiation.

Cutting out the visible light with a wavelength shorter than 720 nm emitted from the infrared lamp by a filter, the removal rate of MO is reduced to 62.5% (Fig. S3), implying that visible light irradiation is more efficient than near-infrared light irradiation in the photodegradation of MO for the $\text{TiO}_2/\text{H}_2\text{O}_2$ thermally-assisted photocatalytic system owing to the higher energy of visible light than that of NIR light.

In contrast to MO, alkali lignin is hardly degraded in the dark in the presence of $\text{TiO}_2/\text{H}_2\text{O}_2$, even at 75°C (Table S1). Meanwhile, the presence of H_2O_2 is requisite for the thermally-assisted photodegradation of lignin although no lignin degradation is detected in the absence of TiO_2 . The $\text{TiO}_2/\text{H}_2\text{O}_2$ thermally-assisted photocatalytic system only decomposes the lignin under light irradiation and elevated temperature (Table S1). Fig. 1 shows the UV-vis absorption spectra of the alkali lignin irradiated for different amounts of time in the presence of $\text{TiO}_2/\text{H}_2\text{O}_2$ under the infrared lamp at 75°C . The characteristic absorption peaks of lignin are located at 205 and 280 nm [20], which are obviously weakened with increasing irradiation time, indicating the degradation of lignin under the thermally-assisted photocatalysis of $\text{TiO}_2/\text{H}_2\text{O}_2$. The calculated degradation rate of lignin based on the variation of lignin absorption at 205 nm (the same below) shows that approximately 70% of the lignin is thermally photodegraded after irradiation for 3 h under the infrared lamp, as shown in the inset of Fig. 1.

To further optimize the thermally-assisted photoreaction conditions, the effects of temperature and H_2O_2 addition level on the degradation rate of lignin were investigated in the presence of 15 μL of H_2O_2 (30% *w/v*) and at a fixed temperature of 70°C , respectively. Fig. 2a shows the UV-vis absorption spectra and degradation

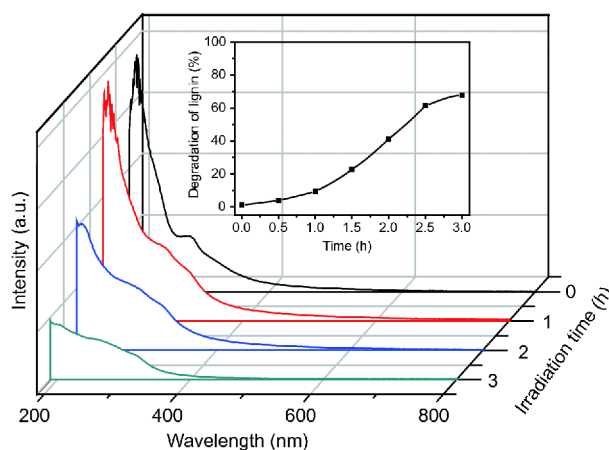


Figure 1 UV-vis absorption spectra of thermally-assisted photodegraded lignin irradiated for different amounts of time with an infrared lamp at 75°C . The charge amount of H_2O_2 (30% *w/v*) is 15 μL . The inset is the degradation rate of lignin as a function of irradiation time.

rate of lignin irradiated for 3 h with an infrared lamp at various temperatures. The addition level of H_2O_2 (30% *w/v*) was fixed at 15 μL . As shown in Fig. 2a, the absorption peak at 205 nm in the UV-vis absorption spectra of the lignin samples significantly decreased with increasing temperature when it is lower than 70°C , indicating an increase in the calculated lignin degradation rate. However, the lignin degradation rate started to decrease when the temperature was higher than 70°C due to the accelerated thermally-assisted decomposition of H_2O_2 . Therefore, the optimal temperature is 70°C for the thermally-assisted photodegradation of lignin in the presence of H_2O_2 .

Fig. 2b shows the UV-vis absorption spectra and degradation rate of lignin after thermally-assisted photodegradation at 70°C for 3 h under an infrared lamp at various H_2O_2 addition levels. As shown in Fig. 2b, the introduction and increase in the addition level of H_2O_2 significantly promoted the thermally-assisted photodegradation of lignin. When the addition level of H_2O_2 was increased to 20 μL , the characteristic absorption band of alkali lignin at 205 nm almost disappeared, indicating a nearly complete degradation of lignin. Therefore, a suitable increase in H_2O_2 addition level improves the thermally-assisted photocatalytic reaction of lignin.

To further explore the role of H_2O_2 in the thermally-assisted photodegradation of lignin, the effects of the addition sequence of H_2O_2 and lignin on the degradation of lignin under an infrared lamp irradiation at 70°C and on the zeta potential of TiO_2 were investigated. Fig. 3a show the thermally-assisted photodegradation curves of

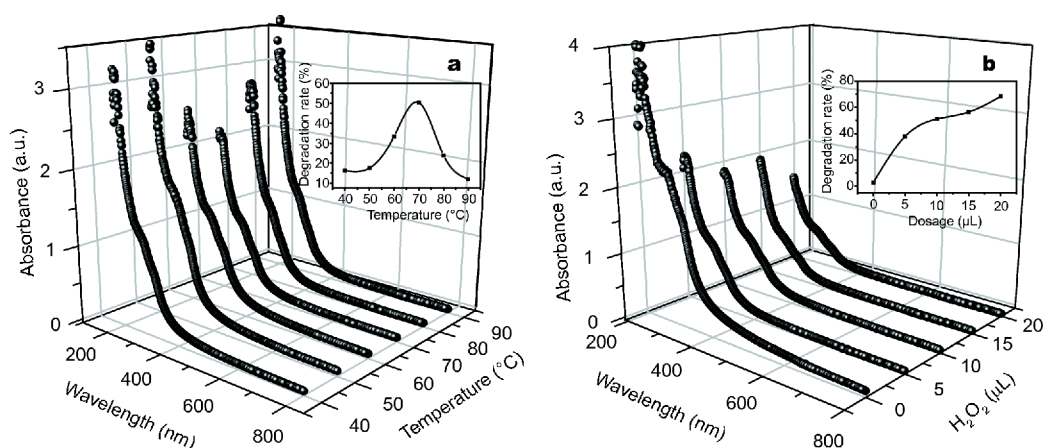


Figure 2 UV-vis absorption spectra of thermally-assisted photodegraded alkali lignin (a) at different temperatures and in the presence of 15 μL of H_2O_2 (30% w/v), and (b) at different addition levels of H_2O_2 and a fixed temperature of 70°C under infrared lamp irradiation. The insets in (a) and (b) are the corresponding degradation rates of lignin calculated based on the lignin absorption at 205 nm.

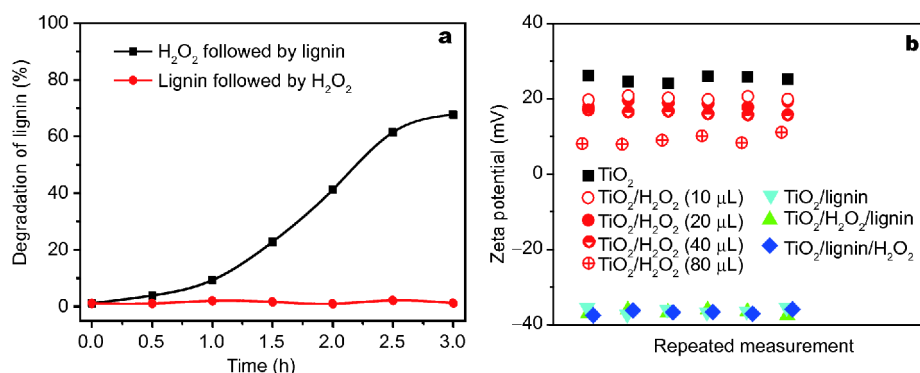


Figure 3 (a) Thermally-assisted photodegradation curves of lignin with different addition sequences of H_2O_2 and lignin with infrared lamp irradiation at 70°C; (b) effects of H_2O_2 and alkali lignin as well as their addition sequence on the zeta potential of TiO_2 . The addition level of H_2O_2 (30% w/v) in (a) is 15 μL .

lignin with different addition orders of H_2O_2 and alkali lignin. The addition level of H_2O_2 is fixed at 20 μL . As shown in Fig. 3a, when the H_2O_2 is added first, the lignin degradation is significantly increased with increasing time under irradiation with an infrared lamp. However, when the H_2O_2 is added after lignin, the lignin degradation rate is hardly changed within 3 h.

The result of the zeta potential measurement, shown in Fig. 3b, indicates that TiO_2 is positively charged, which promotes the adsorption of H_2O_2 and negatively charged lignin. The adsorption of H_2O_2 does not significantly reduce the positive zeta potential of TiO_2 when the addition level of H_2O_2 is lower than 80 μL , while the adsorption of lignin results in the charge reversal of the TiO_2 from positive to negative. Therefore, the addition sequence of H_2O_2 followed by lignin favors adsorption of both H_2O_2 and lignin, while that of lignin followed by

H_2O_2 only favors the adsorption of lignin. These observations indicate that the adsorption of H_2O_2 on TiO_2 plays an important role in the thermally-assisted photodegradation of lignin.

Photoelectrochemical properties of $\text{TiO}_2/\text{H}_2\text{O}_2$ thermally-assisted photocatalytic system

Production of transient photocurrent in a semiconductor indicates the excitation and efficient separation of electrons and holes. To better understand the thermally-assisted photocatalytic activity of $\text{TiO}_2/\text{H}_2\text{O}_2$ under irradiation with an infrared lamp which emits both NIR light and a minor portion of visible light, photocurrent response was measured under both NIR and visible light irradiation at 70°C and compared with that measured at ambient temperature. As the results shown in Fig. 4a and b, TiO_2 cannot produce any photocurrent under NIR

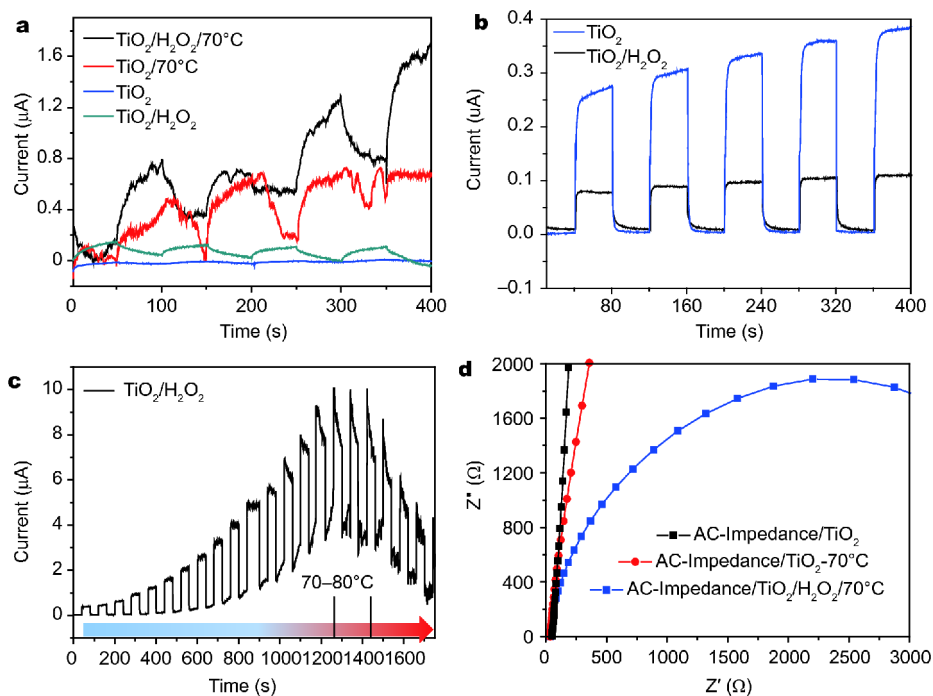


Figure 4 Photocurrent generation on TiO₂ in presence or absence of H₂O₂ under (a) near-infrared light irradiation at either ambient temperature or 70°C, (b) visible light irradiation at ambient temperature; (c) variation of transient photocurrent on TiO₂ with temperature in the presence of H₂O₂; (d) Nyquist plots of the impedance spectra of TiO₂ at ambient temperature, TiO₂ at 70°C and TiO₂ at 70°C in the presence of H₂O₂ in electrolyte solution.

light irradiation at ambient temperature. Even under visible light irradiation, TiO₂ only produces a very weak photocurrent at ambient temperature as a wide gap semiconductor. The presence of H₂O₂ makes the TiO₂ produce a weak photocurrent under NIR irradiation and significantly improves the density of the photocurrent under visible light irradiation at ambient temperature. However, the photocurrent of TiO₂ is still too weak to produce any observable photocatalytic activity, even in the presence of H₂O₂ at ambient temperature.

When the temperature is elevated to 70°C, the TiO₂ produced a rather strong photocurrent, even under NIR irradiation. The introduction of H₂O₂ can further improve the intensity of the photocurrent. Meanwhile, the photocurrent response of TiO₂/H₂O₂ under visible light irradiation is stronger than that under NIR light irradiation. These observations confirm that the thermally-assisted photocatalytic activity of TiO₂/H₂O₂ originates from the thermally-assisted photogeneration as well as high transfer and separation efficiency of photogenerated carriers.

Fig. 4c further shows the variation of the transient photocurrent of TiO₂/H₂O₂ with temperature under visible light irradiation. Apparently, the photocurrent is

gradually enhanced with increasing temperature and reaches its maximum value at 70–80°C. Thereafter, further increasing the temperature leads to a reduced photocurrent. This temperature-induced variation of photocurrent is coincident with the variation of thermally-assisted photodegradation performance of the TiO₂/H₂O₂ thermally-assisted photocatalytic system, further corroborating the importance of the transfer and separation of charge carriers in the thermally-assisted photocatalytic process. Meanwhile, dark current is detected at elevated temperatures, which may be ascribed to thermally-assisted induced carrier generation [21] and H₂O₂-promoted separation of charge carriers [9].

Moreover, electrochemical impedance spectroscopy (EIS) was used to analyze the variation of impedance at the TiO₂ interface with temperature and the introduction of H₂O₂. Fig. 4d shows the Nyquist analysis performed with the three electrode system, in which Ag/AgCl, Pt wire, TiO₂-coated FTO conductive glass and 0.5 mol L⁻¹ Na₂SO₄ are used as reference electrode, counter electrode, working electrode and electrolyte, respectively. As displayed in Fig. 4d, the Nyquist plots of TiO₂ electrode materials cycled in 0.5 mol L⁻¹ Na₂SO₄ electrolyte solution at both ambient temperature and 70°C as well as with or

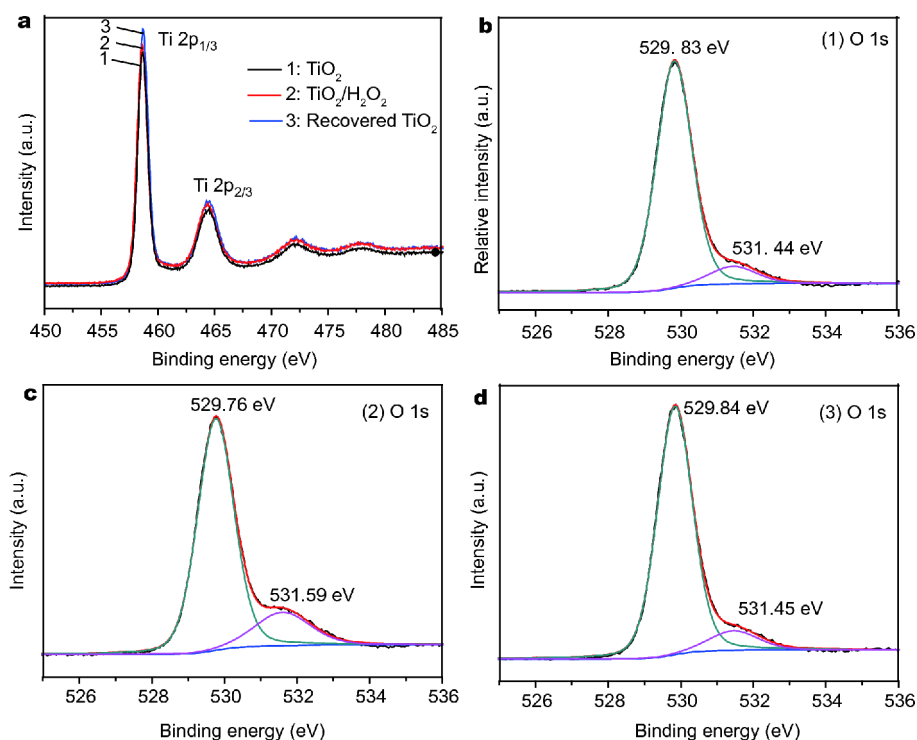


Figure 5 (a) Ti $2p_{3/2}$ of bare TiO_2 , TiO_2 after the adsorption of H_2O_2 and recovered TiO_2 after the thermally-assisted photocatalytic degradation of lignin in the presence of H_2O_2 under infrared lamp irradiation; O 1s core-level XPS spectra of (b) bare TiO_2 , (c) TiO_2 after the adsorption of H_2O_2 and (d) recovered TiO_2 after the thermally-assisted photocatalytic degradation of lignin in the presence of H_2O_2 under infrared lamp irradiation.

without H_2O_2 all show semicircles at high frequencies [22,23]. It is known that the high-frequency arc corresponds to the charge transfer limiting process, which is attributed to the charge transfer resistance at the contact interface between the electrode and the electrolyte solution. The charge transfer resistance can be directly measured as the semicircle diameter [24,25]. The smaller arc in the Nyquist plot of TiO_2 in the presence of H_2O_2 in electrolyte solution at 70°C implies a lower charge transfer resistance due to the presence of H_2O_2 and elevated temperature, further demonstrating that H_2O_2 and elevated temperature can promote the electron transfer at the interface.

Variation of TiO_2 in thermally-assisted photodegradation of lignin

To deeper understand the role of H_2O_2 in the thermally-assisted photodegradation of lignin, XPS spectra were recorded to characterize the variation of surface chemical composition and valence states of TiO_2 before and after adsorption of H_2O_2 as well as after the thermally-assisted photodegradation of lignin in the presence of H_2O_2 . The results are shown in Fig. 5. The Ti 2p core-level XPS spectra of various TiO_2 samples shown in Fig. 5a all ex-

hibit similar symmetrical peaks at 458.5 and 464.3 eV, which are assigned to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of Ti^{4+} in a tetragonal structure [26]. This observation reveals that the TiO_2 is stable in the thermally-assisted photocatalytic process, and no valence variation of Ti^{4+} is observed.

The O 1s core-level XPS spectrum of pristine TiO_2 , as shown in Fig. 5b, displays a strong peak at the binding energy of 529.83 eV and a weak peak at the binding energy of 531.44 eV after deconvolution, corresponding to lattice oxygen Ti–O [27,28] and Ti^{4+} –OH [29], respectively. After treatment with H_2O_2 , the two O 1s peaks shift to 529.76 and 531.59 eV, respectively, and the latter became stronger due to the adsorption of H_2O_2 on the TiO_2 surfaces, suggesting the possible formation of Ti^{4+} – H_2O_2 surface complexes [30]. However, after the thermally-assisted photocatalytic process, the two O 1s peaks shifted back to 529.84 and 531.45 eV, respectively, and the latter became much weaker. This observation suggests that the Ti^{4+} – H_2O_2 surface complexes produced by the adsorption of H_2O_2 were depleted in the thermally-assisted photodegradation of lignin.

Measurement of hydroxyl radicals

Hydroxyl radical species play a key role for the complete

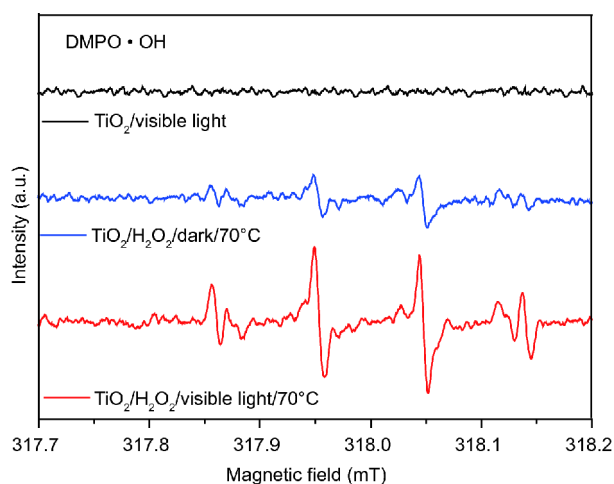


Figure 6 ESR spectra of the DMPO- $\cdot\text{OH}$ radical adduct formed in samples containing 100 mmol L^{-1} DMPO and either 0.1 mg mL^{-1} TiO_2 under infrared lamp irradiation at ambient temperature (black line), 0.1 mg mL^{-1} TiO_2 and 50 mmol L^{-1} H_2O_2 in the dark at 70°C (blue line) or 0.1 mg mL^{-1} TiO_2 and 50 mmol L^{-1} H_2O_2 under infrared lamp irradiation at 70°C .

photodegradation of lignin in a paper mill effluent. ESR was used to detect the production of free hydroxyl radicals ($\cdot\text{OH}$) in the thermally-assisted photocatalytic process, in which 5,5-DMPO was used for trapping the free $\cdot\text{OH}$. Fig. 6 shows the ESR spectra of the DMPO- $\cdot\text{OH}$ radical adduct formed by the reaction of DMPO with $\cdot\text{OH}$ produced in various samples containing either TiO_2 alone, TiO_2 with H_2O_2 under infrared lamp irradiation, in the dark at ambient temperature, or at 70°C .

As shown in Fig. 6, four characteristic peaks of DMPO- $\cdot\text{OH}$ (1:2:2:1 quartet pattern) are observed in the ESR spectra of samples containing TiO_2 and H_2O_2 with a temperature of 70°C . However, the signal recorded under infrared lamp irradiation is much stronger than that recorded in the dark. Meanwhile, the sample in the absence of H_2O_2 has no detectable signal of the DMPO- $\cdot\text{OH}$ radical adduct under infrared lamp irradiation. These observations suggest that $\cdot\text{OH}$ can be produced in the thermally-assisted photocatalytic process of $\text{TiO}_2/\text{H}_2\text{O}_2$ under infrared lamp irradiation, and the light irradiation promotes the production of $\cdot\text{OH}$. The presence of H_2O_2 is necessary for the production of $\cdot\text{OH}$ under infrared lamp irradiation. These observations in combination with the results of thermally-assisted photodegradation, as shown in Fig. 2, demonstrate that the degradation of lignin depends on the production of $\cdot\text{OH}$.

Proposed mechanism of hydroxyl radical production

Based on the results of the above experiments and the

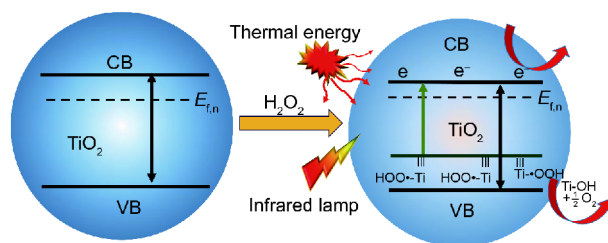


Figure 7 Schematic diagram of charge carrier excitation and transfer processes in $\text{TiO}_2/\text{H}_2\text{O}_2$ thermally-assisted photocatalytic process under infrared lamp irradiation at elevated temperatures.

previous report on formation of $\text{Ti}^{4+}\text{-H}_2\text{O}_2$ surface complexes ($\equiv\text{Ti}\text{-OOH}$) [30], a possible mechanism of charge carrier excitation, transfer and separation was proposed for the production of hydroxyl radicals in the thermally-assisted photocatalytic process. Fig. 7 shows the schematic diagram.

As shown in Fig. 7, as a wide band gap semiconductor, TiO_2 is only excited under UV light irradiation. However, when it was treated with H_2O_2 in aqueous solution, the valence-unfilled Ti^{4+} centers, which occur as $\equiv\text{Ti}\text{-OH}$ on TiO_2 nanoparticle surface, react with the H_2O_2 forming surface complexes of $\equiv\text{Ti}\text{-OOH}$ [30]. The formation of surface complexes extended the optical absorption of TiO_2 to the visible light region due to the electron transition from the surface complexes to the conduction band (CB) of TiO_2 [30]. By further warming the $\text{TiO}_2/\text{H}_2\text{O}_2$ photocatalytic system to temperatures higher than 40°C , electrons are thermally excited from the surface complexes and transferred to the CB of TiO_2 under NIR irradiation. Therefore, at an elevated temperature, such as 70°C , the TiO_2 can be excited after forming surface complexes with H_2O_2 under infrared lamp irradiation, generating electrons and $\equiv\text{Ti}\text{-OOH}$ [30]. The thermally-assisted photogenerated electrons can be directly trapped by the H_2O_2 absorbed on TiO_2 surfaces to form $\cdot\text{OH}$, promoting the separation of the thermally-assisted photogenerated electrons and $\equiv\text{Ti}\text{-OOH}$. The $\equiv\text{Ti}\text{-OOH}$ can further give rise to $\text{Ti}^{4+}\text{-OH}$ and $1/2\text{O}_2$ [30,31]. Increasing the concentration of OH^- causes the reduction of lignin degradation efficiency (Fig. S4), further verifying that the direct trapping of thermally-assisted photogenerated electrons with H_2O_2 is the dominant reaction for $\cdot\text{OH}$ production at neutral pH.

CONCLUSIONS

TiO_2 nanoparticles can act as a thermally-assisted photocatalyst under infrared lamp irradiation at elevated temperatures in the presence of H_2O_2 . The presence of

H₂O₂ and the elevated temperatures facilitate the production and separation of charge carriers, accelerate the carrier transfer at the TiO₂-electrolyte interface and promote the production of hydroxyl radicals under infrared lamp irradiation. The TiO₂/H₂O₂ thermally-assisted photocatalytic system can efficiently degrade lignin in waste water. Suitably increasing the addition level of H₂O₂ and raising the temperature significantly improve the degradation rate of lignin. The optimal temperature for the thermally-assisted photodegradation of lignin is 70°C.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information The set-up of thermally-assisted photocatalytic experiments under infrared lamp irradiation; emission spectrum of infrared lamp; thermally-assisted photodegradation curves of methyl orange catalyzed by $\text{TiO}_2/\text{H}_2\text{O}_2$ at 75°C ; primary investigation on degradation of lignin under various conditions; effect of acid or alkali on thermally-assisted photodegradation of lignin under the irradiation of infrared lamp in the presence of H_2O_2 at 70°C .



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利用 $\text{TiO}_2/\text{H}_2\text{O}_2$ 在可见/近红外光照射下热辅助光催化降解木素

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摘要 木素是一种生物难降解有机物. 造纸工业废水中的木素通常利用诸如 $\text{TiO}_2/\text{H}_2\text{O}_2$ 紫外光催化技术之类的高级氧化技术去除, 但紫外光在太阳光中的份额不足5%. 本文提出了一种 $\text{TiO}_2/\text{H}_2\text{O}_2$ 热辅助可见/近红外光催化技术, 利用该技术可在可见/近红外光照射下将木素有效地催化降解. H_2O_2 在 TiO_2 上的吸附及提高温度可促使光生电子在近红外光和可见光照射下向导带跃迁, 并与 H_2O_2 反应促进光生载流子的分离及羟基自由基的形成. 因此, 提高 H_2O_2 浓度和适当提高温度有助于提高木素的近红外光催化降解速率, 并在 70°C 时获得最大木素降解速率. 本文还根据实验与分析提出了 $\text{TiO}_2/\text{H}_2\text{O}_2$ 热辅助光催化体系降解木素时光生载流子的产生与传递机制.