Photoelectrocatalytic Degradation of Phenol-Containing Wastewater by TiO₂/g-C₃N₄ Hybrid Heterostructure Thin Film

Zhen Wei[†], Fenfen Liang[†], Yanfang Liu[‡], Wenjiao Luo[†], Jun Wang[†], Wenqing Yao[†], and Yongfa Zhu^{†}*

[†]Department of Chemistry, Tsinghua University, Beijing, 100084, China

[‡]China Sinopec Research Institute of Petroleum Processing, Beijing 100083, China

ABSTRACT: TiO₂/g-C₃N₄ (TCN) thin film electrode was fabricated via a surface hybridization and dip-coating method. Phenol could be completely mineralized and the pollutants in coking wastewater could be degraded quickly by TCN under simulated solar light and electric field. The characteristics of the photoelectrocatalytic (PEC) degradation of phenol-containing coking wastewater were investigated under visible light, ultraviolet light and simulated solar irradiation. The results showed that phenol was degraded completely by the TCN-0.3 with a 1.5 V bias in 1.5 h under simulated solar irradiation with 100% TOC removal rate. 45% of the TOC for the coking wastewater was removed by the TCN-0.3 with a 1.5 V bias under 5.0 h simulated solar irradiation, which was 2.45 and 5.69 times as high as that of the pure TiO₂ and g-C₃N₄, respectively. The surface hybrid heterojunction formed between TiO₂ and g-C₃N₄ promotes the migration of the photogenerated electrons and holes and greatly improves the degradation efficiency with applied potential. The significant synergistic effect between the electrocatalytic and photocatalytic oxidation processes in PEC is conducive to electron-hole pair separation, producing the more active substances, such as

hydroxyl radicals, and increases the degree of degradation and mineralization of phenolic compounds.

Keywords: Photoelectrocatalytic; Synergistic effect; Surface hybrid heterojunction; Coking wastewater; Degradation phenolic compounds.

1. Introduction

Coking wastewater is generated from coal coking, coal gas purification, and by-product recovery processes of coking. It contains volatile phenol, polycyclic aromatic hydrocarbons and oxygen, sulfur, nitrogen and other heterocyclic compounds.[1] These compounds are teratogenic, mutagenic and carcinogenic, resulting in the serious toxicity of coking wastewater, which causes serious pollution problems to the whole world.[2] More seriously, phenolic compounds are persistent organic contaminants, exhibiting low biodegradability and thus posing serious and long-term risks to human health once discharged into natural water. Phenol was more difficult to degrade compared to those chlorinated and nitro-substituted phenolic compounds, both of which need to deal with the depth of discharge.[3]

A number of physical, chemical and biological methods have been applied to remove or degrade phenolic compounds in coking wastewater.[4] The conventional treatment process of coking wastewater is the activated sludge process. It consists of solvent extraction of phenolic compounds and steam stripping of ammonia, followed by biological treatment.[5] Since a certain number of refractory and inhibitory organic compounds in coking wastewater are highly concentrated, the conventional activated sludge process is not effective for COD

removal.[6]

Advanced oxidation processes (AOPs) have been the rise of new technologies in the field of water treatment in the last 20 years,[7] which are widely applied to the treatment of bio-refractory organic contaminants in the industrial wastewater.[8, 9] Photocatalysis (PC) is one of the most efficient AOPs. It can produce highly reactive hydroxyl radicals ($\bullet\text{OH}$) to oxidize organic pollutants at ambient temperature and pressure. TiO_2 is widely recognized as the great potential and powerful photocatalyst for its chemical stability, low-cost, eco-friendly and high reactivity.[10] Nevertheless, the TiO_2 utilization efficiency of solar energy was still very low due to the rapid recombination of photogenerated electron–hole pairs and poor response to visible light.[11]

Photoelectrocatalytic (PEC) technology was one of the most popular and effective strategies to inhibit recombination of the electron–hole pairs photogenerated in heterogeneous semiconductor photocatalysis.[12-14] Compared to the pure PC degradation system, the catalyst was immobilized on the conducting substrate to serve as the photoanode in the PEC system. It could be easily separated and recycled after the catalytic reaction.[15] In the PEC process, a potential bias is applied to the photoanode, which provides an external driving force that can promote the photogenerated electrons to move faster through the external circuit to the cathode. Thus, the recombination rate of photogenerated electrons and holes is minimized.[16-18] More importantly, combining the advantages of the heterogeneous PC and electrocatalytic (EC) process, the PEC process is more efficient in degrading organic pollutants and inactivating bacteria compared with both pure PC and EC processes.

To overcome the poor visible light response, numerous approaches have been investigated to improve the visible-light utilization of TiO_2 , such as doping, dye sensitization, heterojunction and hybridization construction and so on.[19-25] Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), as a metal-free conjugated semiconductor photocatalytic material, was first reported for hydrogen evolution under visible light ($\lambda > 420 \text{ nm}$) in 2009.[26, 27] More and more attention has been paid to $\text{g-C}_3\text{N}_4$ because of its high physicochemical stability, outstanding electronic band structure and environmentally benign characteristics.[28-30] $\text{g-C}_3\text{N}_4$ can be combined with many ultraviolet light responsive photocatalysts to enhance their activity under visible light, such as BiPO_4 [31], ZnO [32], and TiO_2 [33]. In spite of these appealing properties, $\text{g-C}_3\text{N}_4$ is difficult to completely mineralize phenolic compounds by itself,[34, 35] limiting its application in the field of environment treatment.

This work composited TiO_2 with $\text{g-C}_3\text{N}_4$ nanosheets to prepare new and efficient $\text{TiO}_2/\text{g-C}_3\text{N}_4$ (TCN) surface hybrid heterojunction structure composites. The morphology, structure, optical and photoelectric properties of TCN were investigated systematically. The effects of $\text{g-C}_3\text{N}_4$ content, the light source and bias voltage on the PEC degradation of phenol and coking wastewater, as well as the TOC removal rate were investigated in detail. The mechanism of the degradation process and the synergetic effect between photocatalysis and electrocatalytic processes were discussed.

2. Experimental

All chemicals were analytical-grade reagents and purchased from Aladdin Chemical Reagent Co., Ltd. and used as received without further purification in the experiments. Indium-tin oxide (ITO) glass (a sheet resistance: 15 Ω/square ; size: 20 mm $\times$ 40 mm;

thickness: 1.1 mm) was purchased from China Southern Glass Co. Ltd.

2.1. Chemical exfoliation of g-C₃N₄:

The metal-free g-C₃N₄ was synthesised by thermally decomposing melamine at 823 K with a ramp rate of 2 K·min⁻¹ in an alumina crucible. Then kept it at 823 K for 4 h in static air and cooled to room temperature naturally. The yellow product was obtained and ground to fine powder for further use.

Chemical exfoliation method was used to prepare g-C₃N₄ nanosheets.[34] The as-synthesised g-C₃N₄ (2 g) was dissolved in 50 mL 98% concentrated sulfuric acid and stirred vigorously for 8 h (the reaction temperature kept at 298 K). Then, the reaction solution was tardily diluted in 500 mL water and sonicated for exfoliation. In this process, large amount of heat was released and the color of the suspension turned to light yellow. Afterwards, the suspension was centrifuged at 2000 rpm for 10 minutes to remove the unexfoliated g-C₃N₄. The procured light yellow product was further centrifuged, washed repeatedly with deionized water to near neutral pH, and dried at 353 K for 24 h. The obtained products were g-C₃N₄ nanosheets.

2.2. Synthesis of TiO₂/g-C₃N₄ Surface Hybrid Compounds:

0.5g of the exfoliated g-C₃N₄ was added into 100 ml of deionized water and then ultrasonically treated for 6 h to form the more stable g-C₃N₄ dispersion. A certain amount of TiO₂ powder (Degussa P25) was added into the dispersion, ultrasonically dispersed for 2 h and stirred for 0.5 h. Then the dispersion was centrifuged and the resulting powder was dried in an oven at 353 K. By grinding the resulting sample, TiO₂/g-C₃N₄ composite photocatalyst

was obtained. They were marked as TCN-X, X labelled as g-C₃N₄ mass ratio in the composite. They were 0.05, 0.1, 0.2, 0.3, and 0.4, respectively.

2.3. Fabrication of the TiO₂/g-C₃N₄ film electrodes:

The TiO₂/g-C₃N₄ film electrodes were fabricated via a dip-coating method on ITO glass.[36] 200 mg of the TiO₂/g-C₃N₄ powder was dispersed in 250 mL water by ultrasonication for 6 h at room temperature. After that, the ITO glass was immersed in the TiO₂/g-C₃N₄ suspension and a typical dip-coating procedure parameters were as follows: the lifting height was 3.5 cm, the dipping time was 60 s and the dipping-pulling rate was 50 μm/s. The dip-coating steps were repeated for three times and the film electrodes were dried for 1 h at 353 K after each dip-coating process. The thickness of TCN-0.3 films reached to 1, 1.5 and 2.5 μm when it was dip-coated one, three and five times, respectively (Figure S4). When dip-coated three times, the PEC degradation activity enhancement most (Figure S5), so the optimal dip-coating steps was three times.

2.4. Characterization:

The morphologies of TCN were examined by electron microscope operated on Hitachi HT 7700 at an accelerating voltage of 100 kV and high-resolution transmission electron microscope (HRTEM) on JEOL JEM-2100F field emission transmission electron microscope operated at an accelerating voltage of 200 kV. FESEM images were characterized on a Hitachi SU-8010 Field Emission Gun Scanning Electron Microscopy. TCN samples were characterized by X-ray diffraction (Rigaku D/max-2400 X-ray diffractometer) with Cu Kα1 (λ = 0.15418 nm) radiation at 40kV and 200 mA to investigate the phase structure.

UV–visible diffuse reflectance spectra (DRS) of TCN were obtained by using Hitachi U-3010 spectrophotometer using barium sulfate as a reference. The room-temperature photoluminescence (PL) spectra of TCN were recorded on Perkin-Elmer LS55 spectrophotometer with an excitation wavelength of 370 nm.

2.5. Degradation activity and PEC measurements:

The EC and PEC measurements were recorded on CHI 660 B (Chenhua, China) electrochemical system workstation. The measurements were conducted in 0.1 M Na₂SO₄ electrolyte solution with a three-electrode cell system. Platinum wire (70 mm in length and 0.4 mm in diameter) was used as the counter electrode and saturated calomel electrode (SCE) was used as a reference electrode. Xenon lamp (500 W) or mercury lamp (15 W, 90% of the energy output at 254 nm) was placed at a distance of 15 cm in front of the film electrodes. The visible irradiation was obtained by the Xenon lamp with 420 nm cutoff filter and the average light intensity was 35 mW/cm². The ultraviolet light intensity was 0.69 mW/cm².

PEC and EC degradation experiments were carried out in a cuboid (5 × 5 × 10 cm) quartz glass reactor. The degraded pollutants were 100 mL phenol with the initial concentration of 5 mg/L or coking wastewater with the initial TOC of 25 ppm. Sodium sulfate was used as electrolyte solution with the concentration of 0.1 M. The film electrodes were submerged 2.5 cm in solutions vertically. 3 mL solutions were sampled every 30 minutes and the particles were separated by high-speed centrifugation and filtrated with a 0.45 μm Millipore filter. The concentration of phenol was detected by the HPLC (Agela Technologies Inc.) analysis with an UV absorbance detector (K 2501) at 270 nm and Venusil XBP-C₁₈ using as a reversed

phase column. The mobile phase was CH₃OH and H₂O (60:40, v/v) with a flow rate of 1 mL/min. The total organic carbon (TOC) was applied to analyse the mineralization degree of organic contaminants on Analytik Jena AG (Multi N/C 2100).

3. Results and Discussion

3.1. Morphology structure and optical properties:

Figure 1A and C are the typical TEM and SEM images of TiO₂/g-C₃N₄ composites (30 wt.% g-C₃N₄). It can be seen the exfoliated g-C₃N₄ samples were very transparent nanosheets, indicating their ultrathin thickness.[34] The HRTEM image of TiO₂/g-C₃N₄ (Fig. 1B) shows the clear lattice fringes of TiO₂ ($d=0.35\text{nm}$ corresponding of TiO₂ (101)), as well as the intimate vague fringes of g-C₃N₄. This intimate contact enables the formation of surface hybrid heterojunction structure between TiO₂ and g-C₃N₄, which is conducive to charge separation.[37] Based on the XRD results, the main diffraction peak of the TiO₂/g-C₃N₄ composite was at $\theta = 25.2^\circ$, which is the characteristic peak of the anatase phase. The intensity of this peak did not change significantly with the increase of g-C₃N₄ content. The (002) plane of the stacking of the conjugated aromatic system in g-C₃N₄ and the diffraction peak of rutile phase (110) plane overlapped at $\theta = 27.4^\circ$. As the content of g-C₃N₄ increased, this overlapped peak became wider and stronger.

Figure 1. TEM (A), HRTEM (B) and SEM (C) images of TCN-0.3; XRD patterns (D) of g-C₃N₄, TiO₂ and TCN photocatalysts.

Figure 2A shows the UV-vis diffuse reflectance spectra of TiO₂, g-C₃N₄ and TiO₂/g-C₃N₄ (TCN). It can be seen that the absorption edge of TiO₂ and g-C₃N₄ are 380 nm and 460 nm, respectively. Based on the calculation results, the band gap of TiO₂ and g-C₃N₄ were 3.26 eV and 2.70 eV, respectively. The band edges of TCN composites were all between that of TiO₂ and g-C₃N₄. Compared with pure TiO₂, the absorption edge of TCN photocatalysts had a red shift with increasing amounts of g-C₃N₄. The band gap of TCN-0.3 was 2.95 eV, expanding to the visible light region. This is attributed to the presence of g-C₃N₄ on TiO₂ surface. Therefore, surface hybrid heterostructure of TiO₂ and g-C₃N₄ was formed in TCN composites.[38, 39]

The recombination rate of free charge carriers can be measured by photoluminescence (PL) spectra.[40-42] Compared with the fluorescence emission spectra (Figure 2B) of g-C₃N₄, the emission peak of TCN-0.3 shown an obvious blue-shift and its intensity decreased significantly. This indicates that electrons can transit from the more negative conduction band of g-C₃N₄ to the conduction band of TiO₂ ($E_{CB, \text{g-C}_3\text{N}_4} = -1.12 \text{ eV}$, $E_{CB, \text{TiO}_2} = -0.5 \text{ eV}$), indicating the formation of hybrid heterojunction structure between g-C₃N₄ and TiO₂ could promote the transfer of photogenerated electrons and holes and thus the recombination of electrons and holes is suppressed.[41, 43]

Figure 2. (A) DRS spectra of g-C₃N₄, TiO₂ and TCN photocatalysts; (B) PL spectra of g-C₃N₄, and TCN-0.3 in different wavelength ranges; (C) Photocurrent measurements under visible light irradiation ($\lambda > 420 \text{ nm}$) of g-C₃N₄ and TCN film electrodes in 0.1M Na₂SO₄ aqueous solution. (D) Potentiodynamic scans

under chopped illumination ($\lambda > 420$ nm) for g-C₃N₄, TiO₂ and TCN-0.3 film electrodes in 0.1M Na₂SO₄ aqueous solution.

3.2. Photoelectric properties:

A bias voltage is applied between the photocatalyst film electrode and the Pt electrode, forming an electric field. Due to this electric field, the photogenerated electrons and holes move in the opposite direction, resulting in their accelerated separation rate, and meanwhile, their recombination possibility reduced. This phenomenon can be detected directly by the change of photocurrent.[44, 45] TiO₂ did not respond to visible light, and its photocurrent was zero. However, the composite responded to visible light obviously. In addition, as the content of g-C₃N₄ increased, the photocurrent increased (Figure 2C). When it increased to 30%, the photocurrent reached the maximum value ($I_p = 3.6 \mu A$). Further increasing the content led to the decrease of photocurrent. This may result from the excessive g-C₃N₄, which agglomeration could hinder the migration and separation of photo-generated electrons and holes.

Figure 2D is a comparison of the linear scan intermittent current among g-C₃N₄, TiO₂ and TCN-0.3. As can be seen, even if the bias voltage is increased, the photocurrent of TiO₂ shows no significant change under visible light. By comparison, the photocurrent of g-C₃N₄ and TCN-0.3 film increased as the bias voltage increased. The bias of the range TCN-0.3 composite wider photocurrent is also larger, indicating that the hybrid heterojunction structure is also conducive to the separation of photo-generated charge, can effectively reduce the photo-generated carriers compound, thereby help to improve its photocatalytic

activity.[46]

3.3. Effect of g-C₃N₄ content on the catalytic activity of TiO₂/g-C₃N₄ photocatalytic:

Due to the high recombination rate of photo-generated electrons and holes, the visible light photocatalytic activity of g-C₃N₄ is not high. As can be seen from Figure 3A, only 8.9% of phenol was removed by g-C₃N₄ after 5 h visible light irradiation. TiO₂ has no photocatalytic activity under visible light. As for g-C₃N₄ and TiO₂ hybrid composite, the degradation efficiency of phenol increased as the content of g-C₃N₄ increased. When the content of g-C₃N₄ increased to 30% (TCN-0.3), the degradation efficiency of phenol reached the maximum of 22.3% under visible light, which is 2.5 times as high as that of the pure g-C₃N₄. Under ultraviolet light, the results are similar. When g-C₃N₄ accounted for 30%, the degradation efficiency of phenol reached the maximum value of 47.6%, which is four times as high as that of the pure g-C₃N₄ and 2.8 times of TiO₂. Further increasing the amount of g-C₃N₄, the photocatalytic degradation activity of the composite decreased and the degradation efficiency of TCN-0.4 was 14.5% under visible light and 41.8% under UV light. When the content of g-C₃N₄ was lower, the number of photogenerated electrons was limited and they are much easier to recombine with a hole. The chemical exfoliation of g-C₃N₄ nanosheets are prone to agglomeration when the g-C₃N₄ content was high, resulting in the reduced reaction active sites and lower photocatalytic activity.[47] Therefore, the optimal ratio of g-C₃N₄ was 30%. At this point, agglomeration of g-C₃N₄ nanosheets is slight and the surface hybrid heterojunction structure forms, which largely contributes to the separation of electron-hole pairs.

Figure 3. (A) Photocatalytic degradation of phenol on various film electrodes in 0.1M Na₂SO₄ solution under visible light ($\lambda > 420$ nm) or UV irradiation ($\lambda = 254$ nm); (B) Electrocatalytic and photoelectrocatalytic (visible light $\lambda > 420$ nm) degradation of phenol on TCN-0.3 electrode at various potentials in 0.1M Na₂SO₄ solution. (The concentration of phenol was 5ppm.)

3.4. Effect of bias potential on photoelectrocatalytic activity of TiO₂/g-C₃N₄:

TCN-0.3 was selected as a typical sample for studying the EC and PEC degradation of phenol. Figure 3B shows the EC degradation efficiency of phenol at different bias potentials in 5 h. The degradation efficiency of phenol gradually increased as the bias potential increased in the range of 0.5-2.5V. When the bias voltage was 2.5V, the EC degradation efficiency of phenol reached the maximum of 90.2%. However, the phenol degradation efficiency decreased when the bias voltage further increased. It dropped to 17.9% at 3.5V bias voltage, which may be due to the formation of phenol-based polymers hindering the further degradation of phenol.[36, 48]

As can be seen from Figure 3B, the EC degradation efficiency of phenol was greatly increased by the visible light. In addition, the PEC degradation efficiency of phenol increased as the bias potential increased in the range of 0.5-1.5 V, and complete degradation of phenol

was achieved when the potential was 1.5 V or higher. The increased degradation efficiency of phenol by the increasing bias voltage can be explained as follows: The bias voltage can increase the width of the space charge layer, which can promote the separation and refrain the recombination of photogenerated carriers. As the voltage increased, the increment of the space charge layer's width increased, and hence the PEC degradation efficiency of phenol increased. However, when the bias voltage was higher than 2.5 V, the width of the space charge layer cannot be further increased, since the electrons generated from the photocatalytic process is constant under fixed light intensity. Therefore, the degradation rate of phenol did not increase when the bias potential was higher than 1.5 V. When the bias voltage higher than 2.5 V, the degradation rate of phenol decreased due to the reallocation of the space charge layer and the Helmholtz layer. This reallocation would result in the reduced the number of photogenerated carriers and thus the decreased degradation rate of phenol. At 3.5 V bias conditions, the degradation efficiency of phenol decreased to 52.8%. Based on the above results, the optimum voltage in this experiment is 1.5V and this voltage is adopted in the following experiments.

3.5. Photoelectrocatalytic mineralization of phenol and coking wastewater:

To study the photoelectrocatalytic degradation efficiency of phenol by $\text{TiO}_2/\text{g-C}_3\text{N}_4$ samples, different light sources were utilized at a bias voltage of 1.5 V. As can be seen from figure S1, S2 and S3, phenol could be completely degraded by TCN-0.3 composite in 2 h' visible light irradiation, 1 h' UV irradiation and 1.5 h' simulated solar irradiation. $\text{g-C}_3\text{N}_4$ or TiO_2 alone requires 3 h or more time to achieve complete degradation of phenol under

different light sources with 1.5V bias potential. As can be seen from the rate constant values of g-C₃N₄, TiO₂ and TiO₂/g-C₃N₄ (Figure 4A), TiO₂/g-C₃N₄ was more efficient than pure g-C₃N₄, and TiO₂ under UV, visible and simulated solar light. Furthermore, to do a simple addition, we can see that the rate constant of TiO₂/g-C₃N₄ was larger than the sum of that of pure g-C₃N₄ and TiO₂. This indicates that the surface hybrid heterostructure formed between TiO₂ and g-C₃N₄ can significantly enhance the activity of TiO₂/g-C₃N₄ composite. The PEC activity of TCN-0.3 under UV irradiation is almost 2.6 times as high as that of TiO₂ and 2.2 times of g-C₃N₄ under visible light. When used Xe lamp to simulate solar irradiation, The PEC activity of TCN-0.3 is 2.88 times of g-C₃N₄ and 2.4 times of TiO₂.

Figure 4. (A) The rate constants for PEC degradation of phenol by g-C₃N₄, TiO₂ and TCN-0.3 film electrodes under different light irradiation conditions; (B) The change of TOC in the PEC degradation of

phenol by g-C₃N₄, TiO₂ and TCN-0.3 electrodes under simulated solar irradiation (full spectrum) and 1.5V bias potential; (C) The change of TOC in the PEC degradation process of coking wastewater by TCN-0.3 electrode under simulated solar irradiation (full spectrum) and 1.5V bias potential. (D)The plots of photogenerated carriers trapping on PEC process by TCN-0.3 under visible light ($\lambda > 420$ nm) and 1.5V bias potential.

As stated earlier, the ability to deep mineralize organic pollutants is crucial for environmental governance. During many EC, PC or PEC processes, phenol was conversed to more poisonous benzoquinone and hydroquinone rather than mineralized to CO₂ and H₂O. In this work, TOC was employed to evaluate the mineralization efficiency of phenol under different experimental conditions. As can be seen from figure 4B, only 32.6% and 54.3% TOC was removed by pure g-C₃N₄ and TiO₂ with 1.5 V bias potential under simulated solar irradiation in 3 h. By comparison, 100% TOC removal rate could be achieved when TCN-0.3 composite were utilized, indicating the improved mineralization degree.

Coking wastewater is a very serious conundrum to the world since it contains strong toxic phenolic compounds, polycyclic aromatic hydrocarbons compounds and so on.[2, 49] To evaluate the efficiency of TCN-0.3 in mineralizing coking wastewater, TOC removal rate was examined in the PEC degradation process of coking wastewater under simulated solar irradiation at a bias voltage of 1.5V. Less than 10.0% of the TOC in coking wastewater was removed by Pure g-C₃N₄and 18.3 % was removed by pure TiO₂. By comparison, 45.0% was removed by TiO₂/g-C₃N₄ composite (TCN-0.3) in 5h (Figure 4C). This result indicates that the surface hybrid heterojunction structure of the composite photocatalyst can enhance the

mineralization efficiency of coking wastewater.

3.6. Synergistic catalytic degradation mechanism:

The main active species of g-C₃N₄ is superoxide radical during the PC process,[50] while holes are the main active species of the TiO₂,[10] so the main oxidation active species of TiO₂/g-C₃N₄ composite may be the hole and superoxide radicals. However, based on the active species trapping results, the main active species were different during the PEC process. The hydroxyl radicals, holes and superoxide radicals during the PEC degradation of phenol over TCN-0.3 were investigated with the addition of tertiary butanol ($\bullet$ OH scavenger)[51], EDTA-2Na (holes scavenger)[52], p-benzoquinone ($\bullet$ O₂⁻ scavenger)[53]. The addition of trapping agents could decrease the PEC degradation rate of phenol with different degree. Among them, tertiary butanol decreased the rate most significantly shown in Figure 4D, indicating that the hydroxyl radicals are the major oxidative species in the mineralization of phenol by TiO₂/g-C₃N₄ composite.

Figure 5. PEC degradation mechanism by TCN-0.3 electrode.

Based on the band gap structure of g-C₃N₄ and TiO₂, the PEC degradation mechanism was

proposed and illustrated in Figure 5. As can be seen, the photogenerated electrons in g-C₃N₄ nanosheets can easily transfer to TiO₂ since the conduction band potential of the g-C₃N₄ is lower than TiO₂. On the other hand, the valence band potential of TiO₂ is higher than g-C₃N₄, and thus the photogenerated holes on the surface of TiO₂ can easily transfer to the valence band of g-C₃N₄. To realize the efficient transfer of photogenerated charge carriers, the formation of surface hybrid heterojunction structure is of great importance. It is crucial in suppressing the recombination of electrons and holes.

On the one hand, the light irradiation promoted the electrocatalytic oxidation. The anodic current density significantly increased with increasing the bias potential and oxygen could be generated when the applied potential was higher than 1.4 V.[54, 55] As an electron acceptor, oxygen could accept electrons and combine with hydrogen ions, producing hydrogen peroxide on the TCN-0.3 electrode (Equation 1). However, the oxidation ability of H₂O₂ was not high enough to completely mineralize phenol. The hydroxyl radicals could be generated through equations (2) and (3), promoting the mineralization of phenols and other organic substances in wastewater.

On the other hand, the photocatalytic efficiency was improved by the bias potential. The photogenerated electrons transferred to the platinum electrode quickly through an external circuit with the assisted electric field. It promoted the photogenerated carriers to spatially

separate and hence reduced the recombination rate of electron-hole pairs. The utilization of holes was improved due to generate hydroxyl radicals on the electrode surface (Equation 3) and preventing the oxidation of the intermediate product restored in the cathode.

4. Conclusion

TiO₂/g-C₃N₄ thin film electrode was fabricated via a surface hybridization and dip-coating method. This composite film was efficient in photoelectric degradation of phenol and wastewater. Under simulated solar irradiation, the TCN-0.3 composite could completely mineralize phenol at a bias voltage of 1.5V in 1.5 h. In addition, 45% of the TOC in coking wastewater was removed in 5 h's solar irradiation which was 5.69 times higher than that of pure g-C₃N₄ (7.9%) and 2.45 times of TiO₂ (18.3%). The enhanced photocatalytic activity and mineralization efficiency of TiO₂/g-C₃N₄ composite are attributed to the formation of surface hybrid heterojunction structure between g-C₃N₄ and TiO₂. This heterojunction can effectively suppress the recombination rate of photogenerated electrons and holes, and thus improves the PEC efficiency. In addition, the synergistic effect between photocatalysis and electrocatalysis significantly improves the degradation and mineralization efficiency of phenolic compounds, making the PEC process an effective method to deal with coking wastewater.

Supporting information available

Additional figures for the the change of phenol concentration in the PEC degradation process by g-C₃N₄, TiO₂ and TCN-0.3 electrodes under different light irradiation and 1.5V bias potential associated with this article can be found in the online version.

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