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Sustainable and continuous removal of trimethylamine in a bio-photoelectrochemical reactor using g-C₃N₄/TiO₂ photocathode with power generation

Jianqing Han, Lifan Liu* and Xuguang Lu

Abstract

BACKGROUND: Trimethylamine (TMA), as a harmful nitrogenous gas, is potentially toxic to animals and human beings. In recent years, the emission of TMA has caused huge environmental problems. TMA is strongly toxic and carcinogenic and requires efficient treatment technology. Photocatalysis and photoelectrocatalysis (PEC) have attracted great interest because of their environmental friendliness and high efficiency. The key problem is how to construct high-efficiency systems and prepare high-activity catalysts.

RESULTS: To eradicate TMA in air, an efficient electrochemical system with bio-anode and photocathode (g-C₃N₄-TiO₂) was designed. It removed TMA in air continuously and efficiently, for both single-cathode and double-cathode systems. This is the first report about TMA removal in such integrated g-C₃N₄/TiO₂ photocathode and bio-electrochemical system. Effects of reaction conditions were investigated, such as the TMA concentrations and flow rates. The highest efficiency for TMA removal was in an integrated PEC and microbial fuel cell (MFC) system with potassium persulfate (PS) activation. The double-cathode PEC-MFC-PS system could remove more TMA (1.9 g m⁻³ h⁻¹ versus 1.3 g m⁻³ h⁻¹) compared with the double-cathode PEC-MFC system.

CONCLUSIONS: A novel TMA treatment system – PEC-MFC system – was constructed, coupling PEC with MFC for continuous removal of TMA from air. Combined with activated PS, a PEC-MFC-PS system was designed and constructed and proved effective in oxidizing gaseous TMA and generating electricity at the same time, which has practical application prospects for the treatment of TMA pollution.

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Keywords: continuous flow; g-C₃N₄-TiO₂ photoelectrocatalytic cathode; bio-anode; trimethylamine removal

INTRODUCTION

Trimethylamine (TMA) is a toxic, nitrogen-containing, volatile organic compound (VOC) blamed for pungent odor emission.^{1,2} Malodorous TMA is difficult to eradicate³ from industrial sources such as livestock manure treatment,⁴ sewage treatment plants,⁵ landfill waste disposal⁶ and fishmeal plants.⁷ At certain concentrations, aerial exposure to aliphatic amines causes respiratory and eye irritations as well as neurotoxic effects and spleen and kidneys damages with 15 ppm of TMA.^{8,9} The Occupational Safety and Health Administration sets the allowable limit of TMA as 10 ppm

operating at ambient temperature, while the oxidation methods operate at room temperature or higher temperature for thermal processes, being high cost and treating low-concentration VOCs. Chemical methods are rarely integrated with biological ones in VOC treatment, until recently with a new process integrating microbial fuel cell with catalytic electrodes that readily remove VOCs by synergetic adsorption and degradation by photo- and electrochemically initiated reactive species.

Use of biofilters is well known as a relatively efficient and cost-effective approach,^{14,15} but they have limitations of excess



room illumination and the detection limit of TMA is 10 ppm for 10 h.¹⁰ The TMA concentrations in waste streams vary in a wide range because of different emission sources, and are often far above 10 ppm.

TMA is strongly toxic and carcinogenic^{11,12} and requires efficient treatment technology. Various strategies with different advantages and restrictions have been adopted, including bio-based ones and physical and/or chemical ones, such as scrubbing, adsorption, condensation and oxidation.¹³ Biotechnology is often of low cost,

biomass accumulation and uneven distribution of biomass and nutrients in treatment of polluted air streams.¹⁶ Photocatalysis

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efficiency declines due to the recombination of photoinduced electron-hole pairs.¹⁷ Continuous efforts have been made to improve the separation of electrons and holes.^{18,19}

Photoelectrocatalytic (PEC) technology effectively inhibits the recombination of electron-hole pairs, and has fast degradation rate, consuming less energy without secondary pollution.²⁰ It needs only low voltage to facilitate the separation of electron-hole pairs to promote redox reactions.^{21,22} A microbial fuel cell (MFC) can generate a certain electric current by bacterial oxidation of gaseous pollutants.²³ Studies have implied that combining PEC and MFC has advantages and greater effects in air purification systems,²⁴ in bio-electricity recovery,²⁵ degradation of organic pollutants²⁶ and continuous hydrogen production.²⁷ Catalyst g-C₃N₄-TiO₂ has been widely investigated recently for the degradation of contaminants.^{28–31} There are few studies yet reporting the removal of pollutants with PEC-MFC-potassium persulfate (PS) systems, especially no reports of VOC emission control or for air purification. Moreover, to the best of our knowledge, the use of g-C₃N₄-TiO₂ materials for PEC-MFC removal of TMA has not been reported.

The aim of the study reported here was to implement enhanced sustainable degradation of TMA in a PEC-MFC system (a bio-photoelectrocatalytic reactor) over g-C₃N₄-TiO₂, and the PEC-MFC-PS system was an innovative system consisting of double-cathode PEC with bio-anode for maximum removal of TMA. The research provides the possibility of combining photocatalysis with MFC to assist the rapid cathodic degradation of gas pollutants and promote power generation at the same time.

EXPERIMENTAL

Materials and chemicals

The materials used included melamine, deionized water, TiO₂ (P25), potassium sulfate (K₂SO₄) and potassium peroxodisulfate (K₂S₂O₈). All chemicals were of analytical grade and were used as received.

Synthesis of catalyst g-C₃N₄/TiO₂

Photocatalyst g-C₃N₄/TiO₂ was prepared via a calcining process. The detailed method was similar to that of a previous report.³² In a typical synthesis, 1 g of P25 powder and a defined amount of melamine were added into 30 mL of distilled water under magnetic stirring to form a suspension and kept for 60 min. The solution was then dried in air at 60 °C overnight to obtain a white mixture, which was sealed in a crucible with a cover and annealed at 550 °C in a muffle furnace (heating rate of 5 °C min⁻¹) for 4 h. For convenience of description, the resulting photocatalysts were labeled as CT_x, where *x* = 1, 2, 3, 4 and 5 denotes that the melamine and P25 were prepared in different proportions with mass ratios of 0.65:1, 3:1, 3.3:1, 4:1 and 6:1, respectively.

Construction of PEC-MFC system

All reactions were conducted in reactor systems made from an acrylic glass at room temperature. The reactors consisted of four parts: pumping, blending, light source and main reaction part. A coated stainless steel mesh with catalyst (cathode) was con-

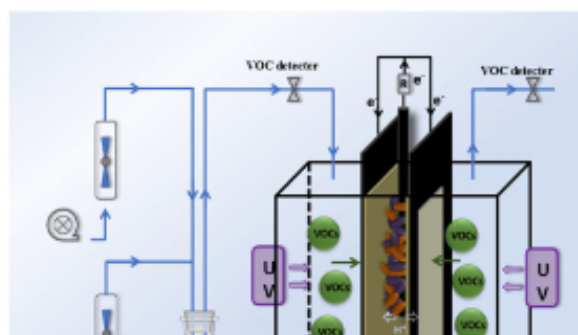
electrogenic microorganisms attached to granular activated carbon. Microorganisms mainly belonged to the genus *Shiwanella* (*Shiwanella* electrogenic bacteria). Electrons were collected by a copper rod in the anode chamber (0.2 cm in diameter) to trigger the PEC oxidation reaction. The copper bar and the g-C₃N₄/TiO₂ cathode through external resistance are connected by insulated copper wire to form a circuit. The changes of current and voltage were measured by a multimeter. Gas flow rate was controlled by gas flow meters. The mixing parts had packed steel balls in a bottle to blend TMA in air. A 5 W UV lamp (wavelength of 365 nm) was used as the light source to vertically illuminate the g-C₃N₄/TiO₂ cathode for reactions. The distance between the UV lamp and the g-C₃N₄/TiO₂ cathode was 4 cm. In Figure 1, the double-cathode system is shown. The single-cathode system was similar to the double-cathode system with only one cathode and one gas chamber.

Characterizations

The surface morphology of the synthesized g-C₃N₄/TiO₂ was observed using scanning electron microscopy (SEM; Nova Nano SEM450, FEI, USA) and elemental composition was measured using energy-dispersive X-ray spectroscopy (EDS). Powder X-ray diffraction (XRD) was conducted with an X-ray diffractometer (XRD-7000S, Shimadzu, Japan; Cu K α , λ = 0.15406 nm) in the range 10–80° with a scan step of 5° min⁻¹. X-ray photoelectron spectroscopy (XPS) data were collected with a scanning X-ray microprobe (ESCALAB250xi, Thermo Fisher). The optical properties of samples were determined with a UV-visible spectrophotometer (Lambda 950, PerkinElmer Management Co. Ltd). An automatic physical adsorption apparatus (Autosorb-iQ-C, USA) was used to characterize the pore structure and surface area. The electrochemical properties were investigated via continuous cyclic voltammetry (CV) with an electrochemical work station (Reference600, China).

Photoelectrocatalytic degradation experiment

The catalyst (0.05 g) as cathode was coated on stainless steel by silica gel solution with an effective coating area of 13.2 cm² (2.4 cm × 5 cm). The material was placed in an oven at 60 °C for drying, and then inserted into the reactor for use. The TMA content was quantified via a gas chromatograph (GC-7900,



nected to the bio-anode with microorganisms to form the PEC-MFC system. A proton exchange membrane divided the PEC-MFC system into two chambers, and the MFC cathode chamber (5 cm × 8 cm × 2 cm) was composed of stainless steel mesh with photocatalyst. The anode chamber of MFC (5 cm × 8 cm × 2 cm) was used for storage of anolyte and

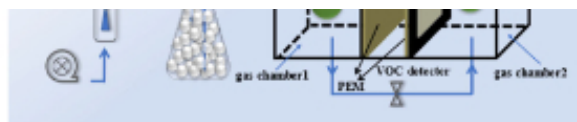


Figure 1. Schematic of the PEC-MFC system.



Techcomp) equipped with a flame ionization detector and an HP-FFAP capillary column (30 m × 0.53 mm × 1.0 μm).

RESULTS AND DISCUSSION

Structure and morphology of catalysts

Morphology and elemental composition of photocatalysts were examined using SEM in conjunction with EDS and transmission electron microscopy (TEM). Figure 2 shows the SEM micrographs of g-C₃N₄, TiO₂ and g-C₃N₄/TiO₂. EDS elemental mapping of g-C₃N₄/TiO₂ and TEM micrographs of g-C₃N₄/TiO₂. The SEM image shows a lamellar structure of g-C₃N₄ (Fig. 2(a)) and uniform nanoparticles of g-C₃N₄/TiO₂ (Figs 2(b) and (c)). The TEM image suggests TiO₂ nanoparticles are embedded in g-C₃N₄ (Fig. 2(d)). In addition, the lattice fringes of the TiO₂ particles can be seen through high-resolution TEM, with a spacing of 0.345 nm, which corresponds to the (101) lattice plane of anatase (Fig. 2(e)). The EDS trace clearly shows the presence of constituent elements in the sample. These results confirm heterojunction formation to achieve improved electron-hole separation.

XRD was used to investigate the phase and crystal structure of g-C₃N₄ and TiO₂ with different weight percentages, as shown in Fig. 3. The TiO₂ phases for the diffraction peaks of samples CT0, CT1, CT2, CT3, CT4 and CT5 were anatase and rutile. Peaks appearing at 2θ = 25.25°, 37.78°, 48.02°, 53.89°, 54.98°, 62.72° and 75.17° can be indexed to (101), (004), (200), (105), (211), (204) and (215) facets of TiO₂ anatase (JCPDS no. 21-1272). The peaks located at 2θ = 27.45°, 36.05° and 56.63° were assigned to the (110), (101) and (200) crystal planes of rutile

TiO₂ (JCPDS no. 21-1276). For pure g-C₃N₄, peaks at 13° (100) and 27.5° (002) can be assigned unambiguously to the in-plane sequential repetition of tri-s-triazine units and interlayer superposition of the aromatic compound respectively (JCPDS no. 87-1526),^{33,34} indicating that the photocatalysts had been successfully synthesized. It can be observed that the positions and intensities of the characteristic diffraction peaks of anatase and rutile show no obvious changes among the various

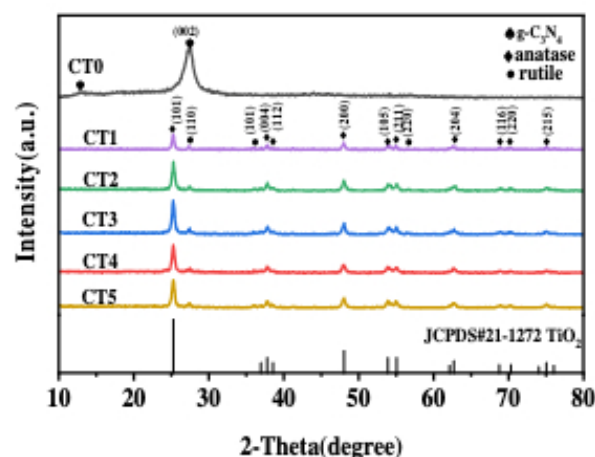


Figure 3. XRD patterns of g-C₃N₄, CT1, CT2, CT3, CT4 and CT5.

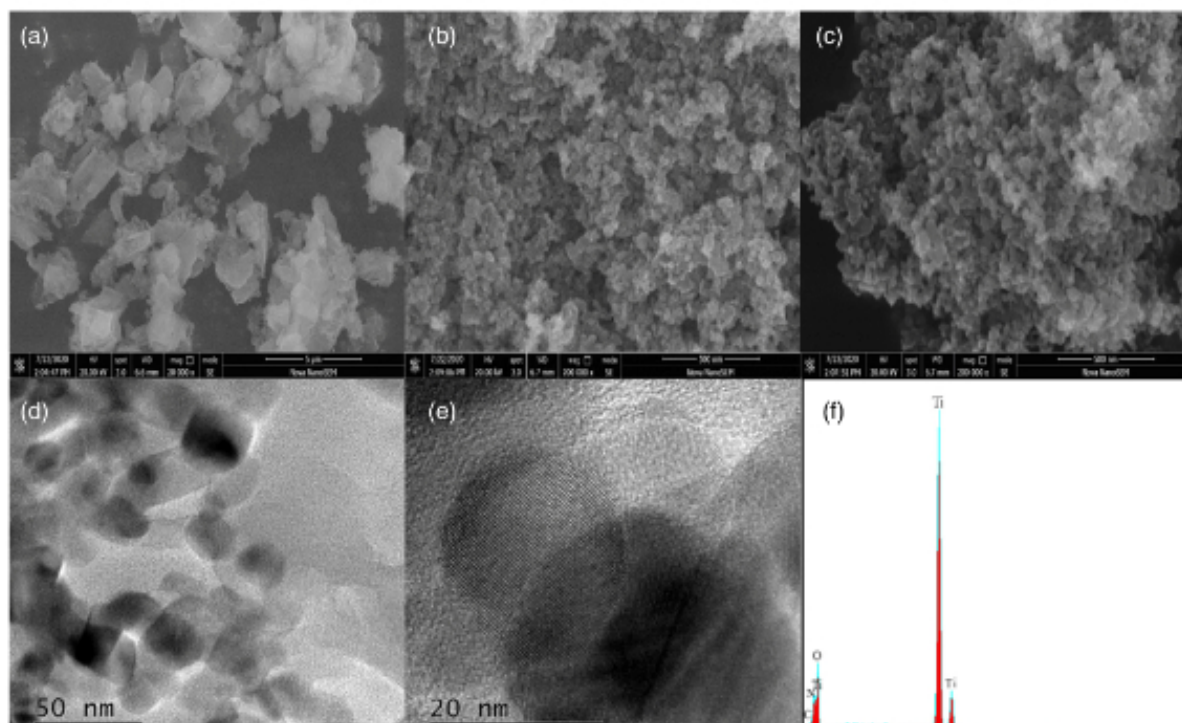




Figure 2. SEM images of (a) $\text{g-C}_3\text{N}_4$, (b) TiO_2 and (c) $\text{g-C}_3\text{N}_4/\text{TiO}_2$. (d, e) TEM images and (f) corresponding EDS elemental mapping of $\text{g-C}_3\text{N}_4/\text{TiO}_2$.

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photocatalysts. By contrast, the presence of $\text{g-C}_3\text{N}_4$ did not have a significant effect on the anatase structure of the prepared photocatalyst.

To investigate the binding energy of all the elements of the as-prepared samples, XPS was used, as shown in Fig. 4. The overall XPS survey spectrum (Fig. 4(a)) suggests C, N, O and Ti elements present in $\text{g-C}_3\text{N}_4/\text{TiO}_2$. In the high-resolution C 1s spectrum (Fig. 4(b)),

two peaks located at 284.5 and 288.0 eV matched with the standard carbon (C–C bonds) and the sp^2 -hybridized carbon (N–C=N).^{35,36} Figure 4(c) shows three peaks centered at 398, 399.5 and 403.87 eV. The first two are attributed to sp^2 -hybridized nitrogen (C–N=C) and tertiary nitrogen (N–(C)₃) groups in the triazine ring, respectively. The peak at 403.8 eV corresponds to the positively charged localized heterocyclic compound (C–N–H).³⁷

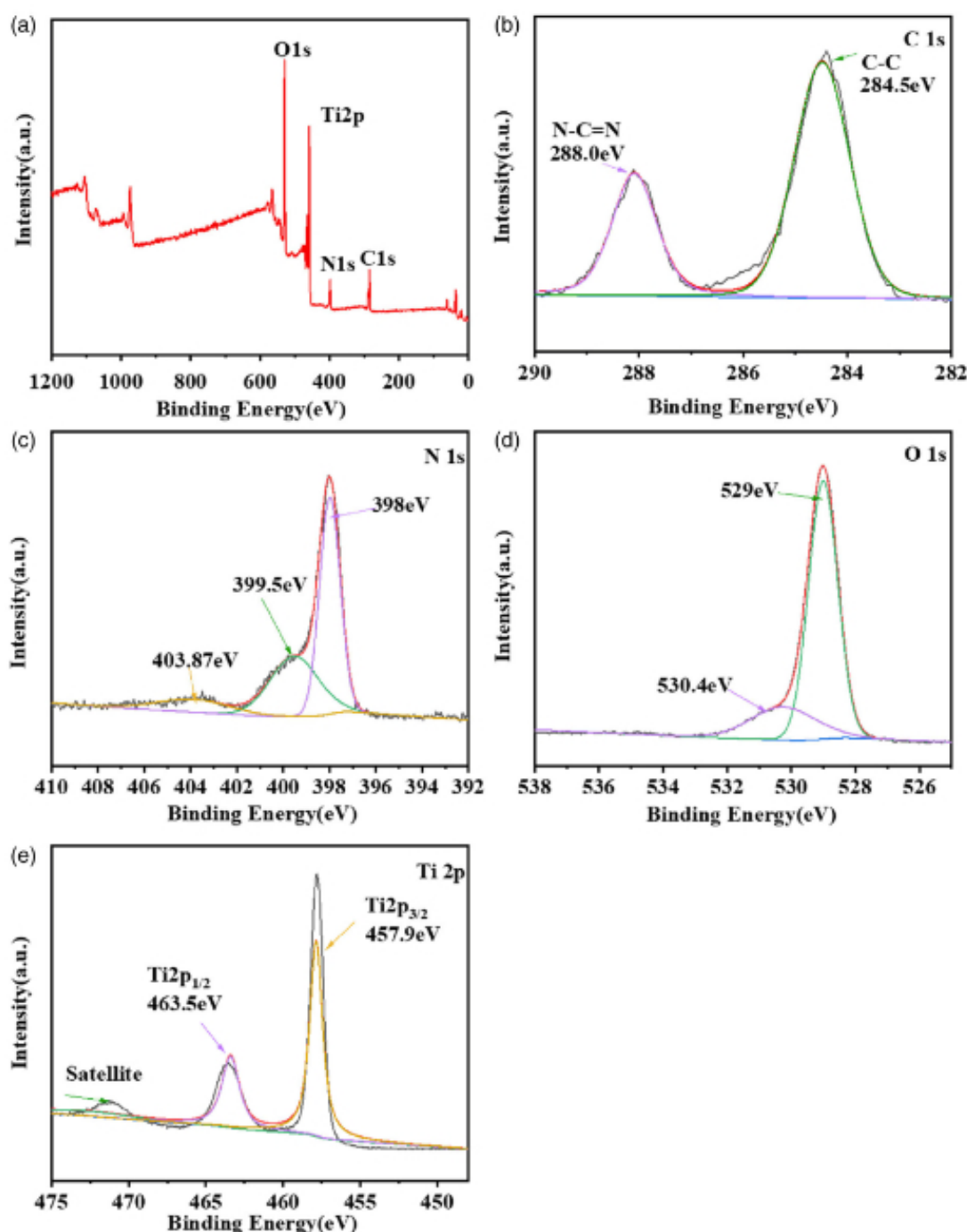


Figure 4. XPS spectra of g-C₃N₄/TiO₂ sample: (a) overall survey XPS spectrum; (b) C 1s; (c) N 1s; (d) O 1s; (e) Ti 2p.

The O 1s XPS spectrum (Fig. 4(d)) indicates the presence of the metal–oxygen bonds in TiO₂ and chemisorbed oxygen³⁸ according to their binding energies of 529 and 530.4 eV. The Ti 2p spectrum in Fig. 4(e) includes two individual peaks, 457.9 and 463.5 eV, consistent with the binding energies of Ti 2p_{3/2} and Ti 2p_{1/2}, respectively.^{34,39} The additional peak at 459.30 eV is attributed to a satellite peak.

Optical and photoelectrochemical properties

In Fig. 5, UV–visible diffuse reflectance spectra show the light-harvesting property for the various samples. Based on Tauc plots, the bandgap values (E_g) of the as-prepared photocatalysts were obtained from plots of $(\alpha h\nu)^2$ versus photo energy. The absorption band edge of g-C₃N₄ nanosheets appeared at 450 nm, corresponding to a bandgap energy of 2.6 eV, which was similar to those previously reported.⁴⁰ The bandgaps of samples varied due to the different contents of g-C₃N₄ on the surface of TiO₂ in the samples. The absorption edge of materials of different proportions is basically at 384 nm from the presence of TiO₂; another edge in the visible range (>460 nm) is from the presence of g-C₃N₄, indicating that g-C₃N₄/TiO₂ could respond to both UV light and visible light for photocatalytic reactions.

A stainless steel mesh was used as a blank control, and the CV curves of that and of samples g-C₃N₄, TiO₂ and g-C₃N₄/TiO₂ were obtained (Fig. 6). A comparison shows that the CV curve of stainless steel mesh has only one oxidation and one reduction peak while those of the other samples have two reduction peaks, which may be due to electrocatalytic reaction. The CV curve of g-C₃N₄/TiO₂ shows the maximum photocurrent density. It shows that the PEC activity is higher after the materials are composited. The current density increases because the g-C₃N₄/TiO₂ composite material can be excited to generate electrons under light, effectively separating photogenerated electrons and holes. The higher current density indicates that the supported catalytic electrode material can transfer electrons faster to reduce the resistance during the charge transfer process. The reversibility of the redox electric pair can be reflected by the difference between the oxidation potential and the reduction potential. The difference of g-C₃N₄/TiO₂ potential is 0.359 mV, which is smaller than that of g-C₃N₄, so the performance is better.

Textural properties

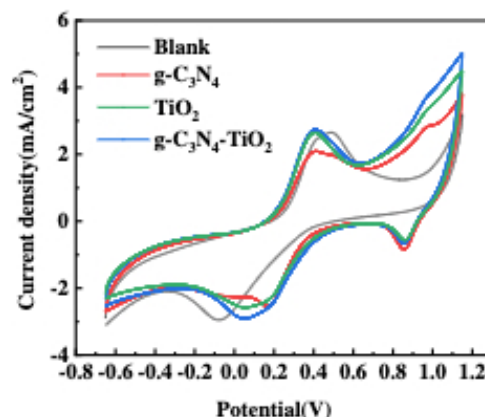
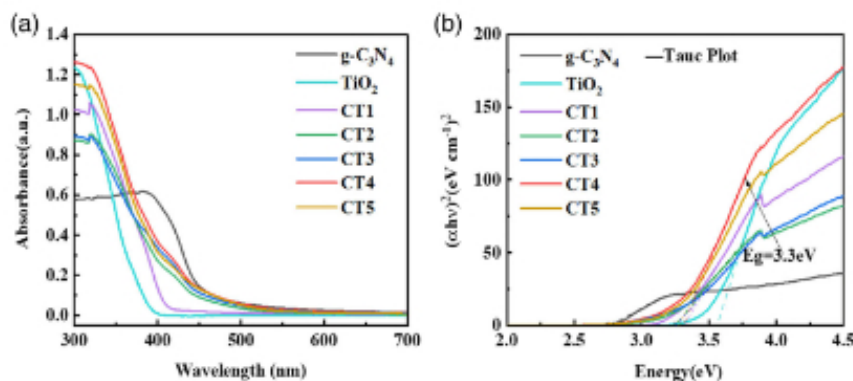
N₂ adsorption–desorption isotherms and pore size distribution (inset) are illustrated in Fig. 7 and the corresponding textural

properties are listed in Table 1. N₂ adsorption–desorption analysis (Fig. 7) demonstrates that all as-prepared samples displayed classical type-IV isotherms with H₃-type hysteresis loops in the high relative pressure range of 0.6–1.0, indicating formation of mesoporous structure.^{41,42} Mesopores play an important role in improving the photocatalytic effect which can accelerate the diffusion of reactants and products in the photocatalysis process and improve the rate of photocatalytic reaction. The curves of pore size distribution were obtained from the Barrett–Joyner–Halenda method. It is found that the maximum particle size distribution was 1–10 nm, which confirmed the nanostructure. Brunauer–Emmett–Teller analysis (Table 1) shows that catalyst CT4 has the highest specific surface area (199.84 m² g^{−1}), about six times higher than that of pure g-C₃N₄ (35.138 m² g^{−1}), suggesting its excellent porosity for exposing more reaction sites for photocatalytic TMA degradation with an appropriate ratio of g-C₃N₄. This result is consistent with the SEM analysis.

Test of different systems for TMA degradation

TMA removal performance of single-cathode system

Series of tests were applied to verify the optimized performance of the photocatalytic system in removal of TMA gas. To understand the changes in gas TMA concentrations over time, we performed different control experiments and each experiment was

**Figure 6.** CV curves of blank, TiO₂, g-C₃N₄ and g-C₃N₄/TiO₂ (CT4) in 1 mmol L^{−1} K₃Fe(CN)₆/0.1 mol L^{−1} KCl electrolyte at −0.65 to 1.15 V.**Figure 5.** (a) UV–visible absorption spectra and (b) corresponding Tauc plots of different samples.

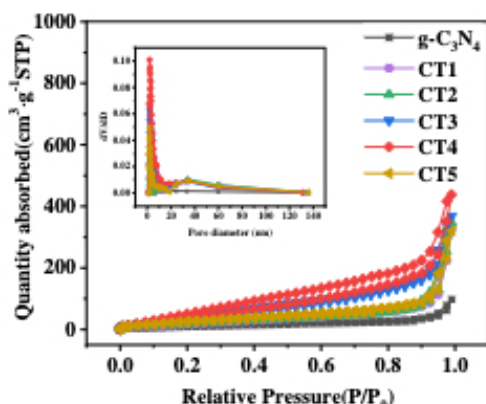


Figure 7. N₂ adsorption-desorption isotherms and pore size distribution (inset) of g-C₃N₄ and all g-C₃N₄/TiO₂ samples.

Table 1. Textural properties of various samples

Sample	S_{BET} (m ² g ⁻¹)	V_p (cm ³ g ⁻¹)	d_p (nm)
g-C ₃ N ₄	35.14	0.17	2.25
CT1	73.55	0.54	2.39
CT2	78.80	0.56	2.25
CT3	130.97	0.64	2.13
CT4	199.84	0.78	2.00
CT5	87.06	0.53	1.75

S_{BET} , Brunauer-Emmett-Teller specific surface area; V_p , pore volume; d_p , average pore size.

repeated three times. EC, PC, EC-MFC, PEC and PEC-MFC represent the treatment of TMA by electrocatalysis, photocatalysis, electrocatalysis with microbial fuel cell, photoelectrocatalysis and photoelectrocatalysis with bio-electrochemical system, respectively. All catalytic capacity evaluations were carried out at the same temperature and the gas flow rate was set to 20 mL min⁻¹ (1.2 × 10⁻³ m³ h⁻¹). The initial concentration was 1.5 g m⁻³. Figure 8(a) shows the profiles of time course and concentration change for catalyst CT4 in comparison with the control samples in PC system. Data show that all samples except g-C₃N₄ are capable of TMA degradation under UV light, because all nanoparticles are positive in UV light absorption (Fig. 5). TMA concentration in effluent gradually increases over time possibly due to catalyst poisoning or property decline when TMA is continuously introduced. Furthermore, the removal of TMA gas was 80–85% for an appropriate ratio of g-C₃N₄/TiO₂ (catalyst CT4), but the removal using pure TiO₂ and pure g-C₃N₄ was significantly lower.

The profiles of oxidative removal of TMA versus time for catalyst CT4 under different external resistance are shown in Fig. 8(b). The reason for exploring the effect of external resistance is because it affects the photocatalytic efficiency by regulating and controlling the amount of electrons transferred from the anode to the cathode.⁴³ The best oxidative removal was obtained at external resistance of 1000 Ω, with an average of about 87% of TMA removal lasting 2 h, followed by a decrease of removal under 10 000, 100 and 10 Ω, which reveals the effect of resistance in the EC system. At 1000 Ω, both the electric current and cell voltage are appropriate

to allow stable operation, and better efficiency. Higher resistance than this reduces the current to lower level, thus reducing the cathode catalysis and TMA removal. While at lower resistance than this, the current is greater, but cannot last long, and therefore is not good for stable operation and better TMA removal.

The initial TMA concentration influences the degradation efficiency. As shown in Fig. 8(c), for PEC systems, as the initial TMA concentration increases from 1.5 to 6 g m⁻³, the corresponding degradation rate gradually decreases from approximately 99% to 80%, indicating that the TMA removal efficiency decreases with an increase of initial TMA concentration. This mainly occurs because at the same catalysis dosage, the same amount of photo-generated electron-hole pairs is generated. So when the initial TMA concentration is higher, the reactive oxygen species supplied by the g-C₃N₄/TiO₂ PEC system is inadequate and, as a result, not improving TMA removal.

The TMA removal processes under different device conditions (EC, PC, PEC, EC-MFC and PEC-MFC) and electricity production were further investigated (Fig. 8(d)). It is observed that the removal rate of TMA gas increased significantly with light irradiation compared with dark adsorption. The oxidative removal of TMA through EC is more rapid than PC and it can reach 89% with continuous flow of gas. Adsorption removal of TMA was stable at 70–80% in 120 min. In the experiment, when the TMA concentration stabilized and reached the adsorption-desorption equilibrium the degradation experiments were started.

It can be observed that the TMA removal using PEC is significantly higher than that using EC, PC and EC-MFC. In Fig. 8(e), the cell voltage for EC-MFC exceeds that for PEC, suggesting that photocatalysis of the material is better. And the removal of TMA gas was further enhanced in the PEC-MFC system at 0.27 V, which suggests the combination of PEC cathode with bio-anode could enhance the power generation capacity of MFC, which is consistent with previous reports.^{26,44} Therefore, the PEC-MFC system can quickly and effectively remove TMA in an extended period of time. And it is far more efficient than previous reports.⁴⁵

Double-cathode PEC-MFC system performance in removal of high-flow TMA gas

To assess the PEC-MFC activity, we increased the flow rate of TMA in the double-cathode PEC-MFC system (catalyst dosage of 0.05 g on each cathode). Figure 9(a) indicates that the TMA degradation rate was about 96%, 98% and 70% when the flow rate was 20, 100 and 120 mL min⁻¹. This is because the full capacity in removal has not been exploited at 20 and 100 mL min⁻¹, while at 120 mL min⁻¹, the change in shortened residence time affects the removal, and could not take full use of the removal capacity to fully adsorb, penetrate and be oxidized in the anode and cathode. Significant change takes place due to the shortened residence time at 120 mL min⁻¹, which was beyond the possible residence time range of completing absorption-adsorption, and disturbing the balance of adsorption-desorption, possibly decreasing the thickness of stagnant layer over the cathode. Also, the capacity of oxidation reaction kinetics is changed and exceeded.

Below 100 mL min⁻¹, such adsorption-desorption and oxidation still could manage to be completed. Figure 9(b) shows the stability of as-prepared samples under a flow rate of 100 mL min⁻¹ within 120 min using CT4. In the first two cycles, TMA removal can reach 99% and there are no obvious changes, while it decreased to 86–90% in the third cycle. This reveals that the photocatalyst has good stability in practical application, because the external electrons generated by the bio-anode from

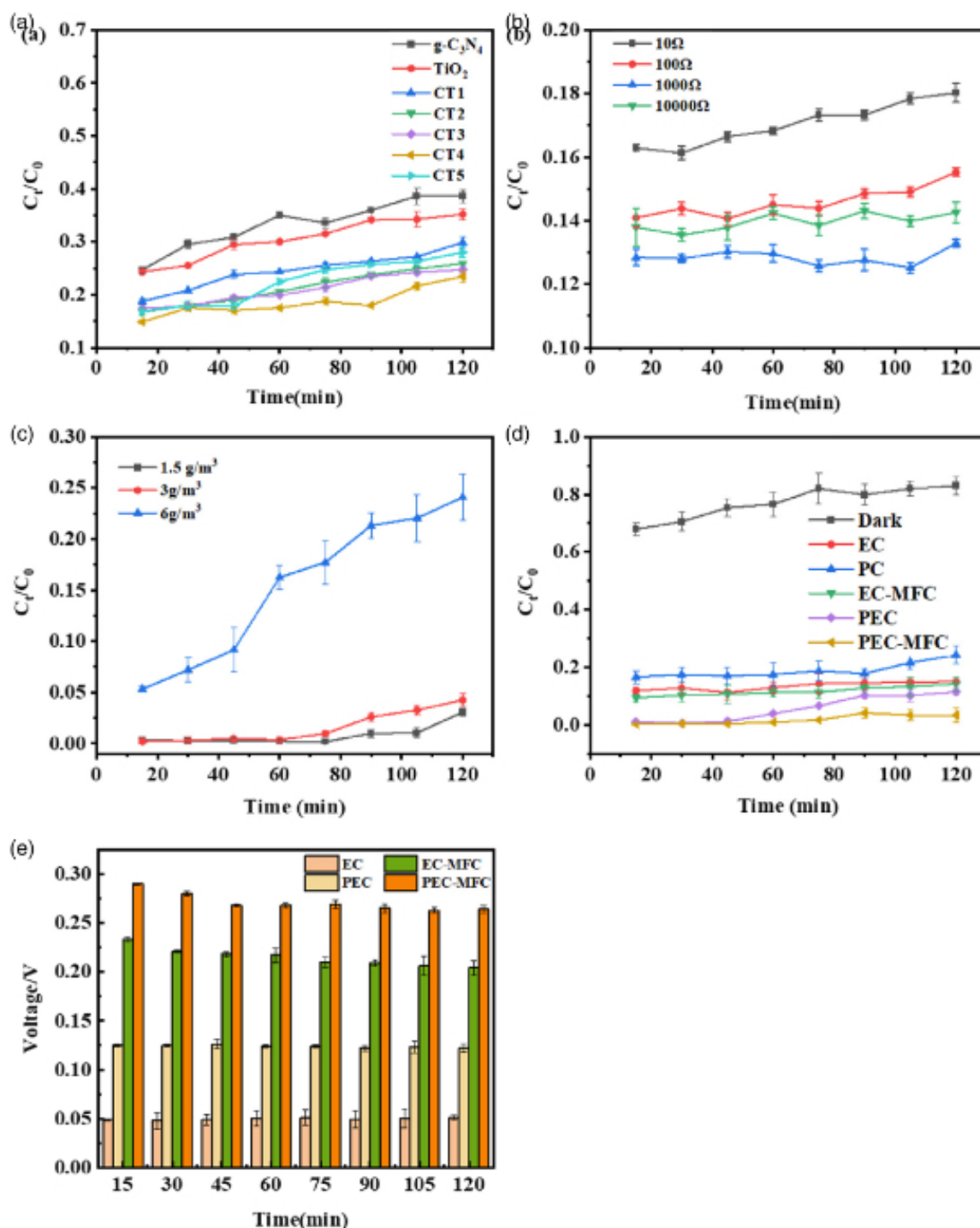


Figure 8. (a) Time courses of TMA removal for $g-C_3N_4$, CT1, CT2, CT3, CT4, CT5 and TiO_2 catalyst samples for PC system. (b) Effect of external resistance on EC system. (c) Effect of different TMA concentrations on PEC system. (d) Different systems with CT4 catalyst. (e) Voltage values of EC, PEC, EC-MFC and PEC-MFC. (C_0 , initial concentration; C_t , concentration at time t .)

the assisted MFC suppress recombination of electrons and holes, and improve quantum yield by accelerating charge and proton transfer on the cathode of the PEC-MFC.²⁴

In order to be more practical, the degradation performance of TMA at higher flow rates was studied. Persulfate activation over the electrode in synergy with the photoelectrochemical catalysis

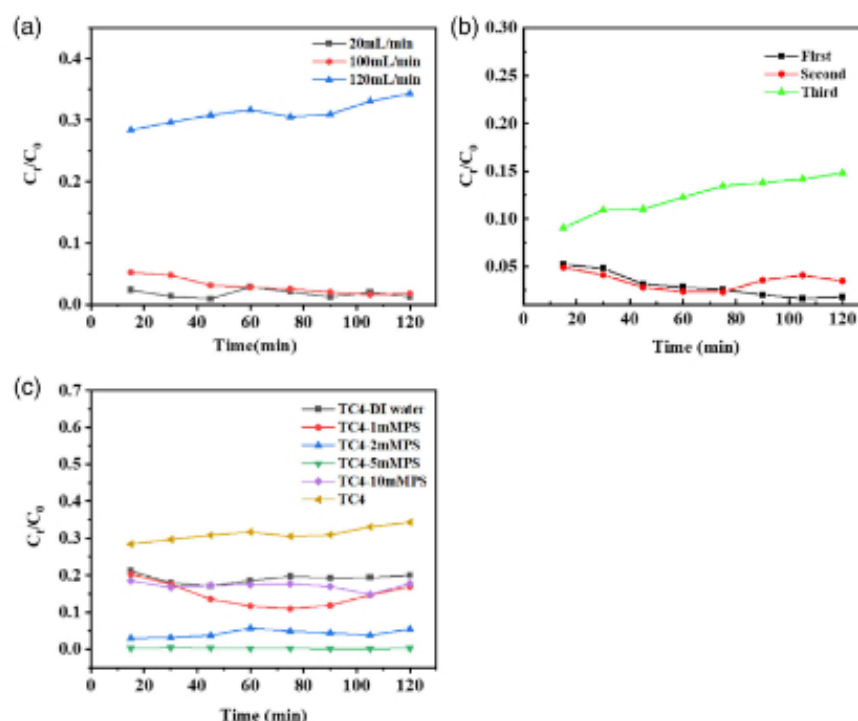


Figure 9. (a) Effect of flow rate on PEC-MFC system. (b) Recycling tests of CT4 at flow rate of 100 mL min^{-1} . (c) Effect of different PS concentrations on TMA removal.

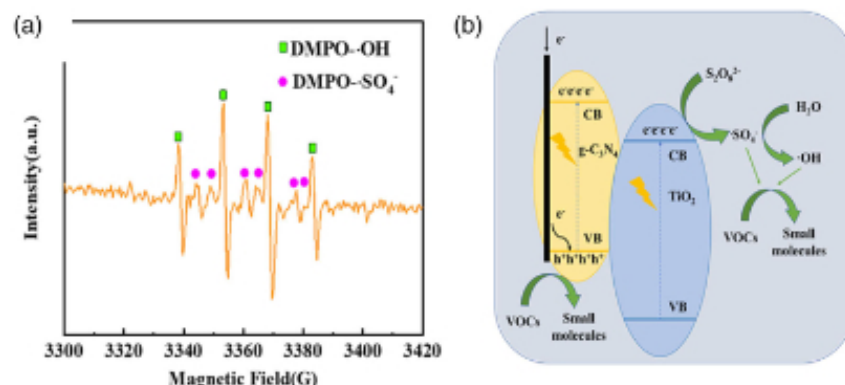
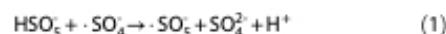


Figure 10. (a) DMPO spin trap EPR spectrum of $g\text{-C}_3\text{N}_4/\text{TiO}_2$ when PS is added. (b) Possible mechanism for enhancing the removal of TMA.

increased efficiency for gas pollutant oxidation. The results in Fig. 9(a) show that TMA was basically completely removed at a flow rate of 100 mL min^{-1} , while the removal was slightly less at a flow rate of 120 mL min^{-1} . The influence of PS on removal performance at different concentrations was explored. The blank was deionized water without PS added. PS entered the two cathode chambers and flowed out from the other end at the same speed, when the flow rate was controlled at 120 mL min^{-1} . Also, it is interesting to note that the performance of the PEC-MFC-PS system is much better than that without PS. The oxidative removal of TMA is rapid in the first 75 min in 1 mmol L^{-1} PEC-MFC-PS; then it markedly decreased later. This may be due to the decrease in PS concentration, resulting in less activated species. Both 2 and 5 mmol L^{-1} PS addition contribute to the fast removal of TMA,

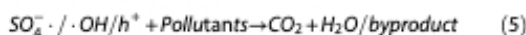
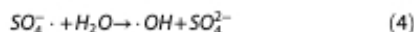
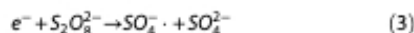
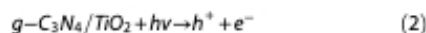
while 5 mmol L^{-1} MPS maintained reaction activity constant. The removal of TMA gas was enhanced by PEC-MFC and integrated PS, accelerating the generation of oxidizing radicals ($>99\%$ TMA removal at $1.9 \text{ g m}^{-3} \text{ h}^{-1}$). However, when 10 mmol L^{-1} PS was added, the TMA degradation efficiency was reduced, which could be attributed to that the dosage of the CT4 photocatalyst will be a limiting factor when the concentration of PS added is much higher. There is not enough catalyst in the system to generate electrons to activate PS. In addition $\text{SO}_4^{\bullet-}$ will react with deactivated PS (Eqn (1)), which reduces the number of oxide species, thereby affecting the degradation efficiency⁴⁶:



Proposed mechanisms

We have demonstrated that excellent TMA removal can be achieved by extending the reaction cathode surface area in the double-cathode system, or further by integrating PS in the cathode. The reason for the enhanced reaction by the composite catalyst CT4 is the high surface area, which means high adsorption property and many active sites for PEC and PEC-MFC system using catalyst CT4, which also enhances activation of PS in the PEC-MFC-PS system. An electron paramagnetic resonance (EPR) determination of the groups that specifically react in the reaction system was carried out. It was found that under UV light, $\cdot\text{OH}$ radicals and sulfate radicals ($\text{SO}_4^{\cdot-}$) can be captured by an aqueous solution of DMPO in PEC-MFC-PS. Usually, because the conduction band (CB) of TiO_2 is lower than that of $\text{g-C}_3\text{N}_4$, there is enough Gibbs free energy to induce electrons from $\text{g-C}_3\text{N}_4$ to be injected into TiO_2 , which is helpful for separating electron-hole pairs.⁴⁷

The electrons in $\text{g-C}_3\text{N}_4$ (CB) are easily transferred to TiO_2 (CB), and the holes in TiO_2 (valence band (VB)) are also easily transferred to $\text{g-C}_3\text{N}_4$ through interface interaction. As a result, the recombination of photogenerated electrons and holes is suppressed.⁴⁸ Under UV light, both TiO_2 and $\text{g-C}_3\text{N}_4$ are excited by light to generate electrons and holes (Fig. 10(a)). The EPR signals shows that $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ exist in the $\text{g-C}_3\text{N}_4/\text{TiO}_2$ -PS photocatalytic system. In addition, the intensity of the signal of DMPO- $\cdot\text{OH}$ is much higher than the signal of $\text{SO}_4^{\cdot-}$, indicating that $\cdot\text{OH}$ plays a more important role than $\text{SO}_4^{\cdot-}$. Secondly, superoxide $\text{O}_2^{\cdot-}$ was not found, because photogenerated electrons tend to react with PS, which makes it difficult for electrons to react with O_2 to produce $\text{O}_2^{\cdot-}$.⁴⁹ The degradation mechanism can be expressed by equations (2)–(5):



CONCLUSIONS

We successfully constructed a double-cathode PEC-MFC synergistic system integrating PEC and MFC processes, which displayed a high performance in removal of TMA under UV light. The TMA oxidation performance in the double-cathode reactors of PEC-MFC and PEC-MFC-PS is stable. MFC provides electrons to the heterojunctions of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and promotes the separation of photogenerated carriers, playing an important role in the degradation of TMA. Strong signals of hydroxyl radicals and sulfate radicals were detected using EPR in the $\text{g-C}_3\text{N}_4/\text{TiO}_2$ -PS photocatalytic system, proving effective PS activation and high-efficiency pollutant degradation capacity. This study presents an efficient and also cost-effective platform for degrading other gas pollutants via the PEC-MFC system. This new system, having higher capacity than PC or pure MFC or biofilter processes, can be considered as integrating the advantages of PC and bio-electrochemical processes, while overcoming the disadvantages. The overall cost will be lower and affordable for practical application.

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