H$_2$O$_2$ Assisted Photoelectrocatalytic Oxidation of Ag-Cyanide Complexes at Metal-free g-C$_3$N$_4$ Photoanode with Simultaneous Ag Recovery

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Supporting Information

ABSTRACT: A g-C$_3$N$_4$ thin film was synthesized by a liquid-based reaction onto ITO substrate via the calcination treatment. The resultant electrode was used as photoanode for photoelectrocatalytic (PEC) oxidation of Ag cyanide complexes with simultaneous Ag recovery, which was enhanced with the addition of H$_2$O$_2$. Surface variation of the g-C$_3$N$_4$ photoanode and titanium cathode was analyzed using SEM, XRD, and XPS techniques. It was observed that, with the cyanide oxidation, Ag oxides and metal Ag were deposited onto the g-C$_3$N$_4$ photoanode and titanium cathode, respectively. The photoelectrochemical response of the g-C$_3$N$_4$ photoanode was obviously increased after the AgO deposition. ESR and trapping experiments confirmed the existence and roles of $^\bullet$O$_2^-$ and $^\bullet$OH in the PEC oxidation process. The photogenerated electrons from g-C$_3$N$_4$ could be captured by $^\bullet$O$_2^-$ and H$_2$O$_2$ generating $^\bullet$OH radicals for oxidizing the Ag cyanide complexes. Meanwhile, the deposition of AgO species onto the g-C$_3$N$_4$ surface increased its electrical conductivity and the migration rate of the photogenerated electrons. Deposited AgO can also enhance the production of active radicals, leading to an increased PEC activity toward the cyanide destruction.

KEYWORDS: Ag cyanide complexes, g-C$_3$N$_4$, Photoelectrocatalysis, Metal recovery, Visible light

INTRODUCTION

The silver cyanides from the photographic, electroplating, and mining industries need to be carefully treated. 1,2,16 Numerous methods, including activated carbon adsorption,17 ferrate oxidation,18 and alkaline chlorination,19 have been investigated for the removal of cyanide from contaminated water. In these processes, the removal of metal cyanide complexes was not complete and the byproducts needed to be treated carefully.1 In this process, an external electrical bias was applied to inhibit the recombination of photogenerated electron–hole pairs. As a result, the photocatalytic activity of the semiconductor photocatalyst was increased.14,15 The PEC process has been largely investigated for its application in the removal of refractory organics and pathogenic microorganisms as well as in water splitting.16–18 In our previous work, PEC oxidation of metal complexes such as Cu-EDTA and Cu cyanides was performed with the prepared TiO$_2$ photoanode. And Cu recovery onto the cathode was achieved by the cathodic reduction.19

Recently, polymeric graphitic carbon nitride (g-C$_3$N$_4$) has been given much attention as a promising photocatalytic material.20–23 With an optical band gap of 2.70 eV, g-C$_3$N$_4$ showed a response to visible-light up to 460 nm. Most of the research focused on the g-C$_3$N$_4$ powders, while a direct and continuous g-C$_3$N$_4$ layer was preferred for the electrochemical or photoelectrochemical applications.24,25 Application of the g-C$_3$N$_4$ electrode as the photoanode for phenol degradation under
visible light irradiation was investigated; it was demonstrated that phenol can be depleted by the g-C₃N₄ under 2.5 V with a total organic carbon removal of 89.3%.²⁶

Herein, a g-C₃N₄ thin film was synthesized by a liquid-based reaction onto ITO substrate during the calcination treatment at 500 °C and used as a photoanode to treat the Ag cyanide complexes by a PEC process under visible light irradiation. Addition of a given amount of H₂O₂ was found to enhance the PEC oxidation of Ag cyanide complexes. With the repeated use of the g-C₃N₄ photoanode, a remarkable enhancement in the PEC oxidation efficiency of cyanide in the presence of H₂O₂ was observed. It was proposed that the generated "O₂•−" and "OH radicals can oxidize Ag(CN)₂⁻ to CN⁻, and the photo-generated electrons to the cathode can be captured by O₂ or H₂O₂ generating more "O₂•−" and "OH radicals, which facilitated the destruction of cyanide as well as the Ag recovery.

**Experimental Section**

Materials. Cyanuric acid (>98%) and benzoguanamine (>98%) were purchased from Tokyo Kasei Kogyo Co., Ltd. AgNO₃ and NaCN (analytical grade) were provided by Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). All the reagents were used without further purification. Indium tin oxide (ITO) conductive film glasses with a size of 10 × 2.5 × 0.2 cm were obtained from Shenzhen Jingweite Technology Co., Ltd. (Shenzhen, China).

Preparation of a g-C₃N₄ Film Electrode. The precursor powder was prepared by a combustion hybrid method, and the g-C₃N₄ film electrodes were prepared via liquid-based growth reaction as described by Xu et al.¹ In a typical process, cyanuric acid and benzoguanamine at molar ratio of 1:1 (about 4 g) were dispersed in 40 mL of deionized water and stirred at 500 r/min for 6 h. The white suspension was then centrifuged at about 7500 rpm to obtain the solid, which was frozen for 24 h and dried at −55 °C for 48 h. As a result, the precursor powder was obtained.

One piece of ITO glass was put in a quartz crucible with the conducting side up, and then an adequate amount of dried precursor powder was transferred to a crucible, totally covering the substrate placed at the bottom. Following, the crucible was then capped and heated at 500 °C for 2 h with an ambient temperature of 3 °C/min in a nitrogen atmosphere.

Photoelectrochemical Experiments. PEC degradation experiments were carried out with a three-electrode system controlled by an electrochemical workstation (CHI660D, Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). The g-C₃N₄ photoelectrode, saturated calomel electrode (SCE), and titanium plate were employed as the counter and reference electrodes, respectively. Pt wire was used as the working electrode and 0.5 mM Na₂SO₄/NaClO₄ aqueous solution at a rate of 10 mV/s⁻¹ was used as the electrolyte. The photo currents density was 0.5 mA/cm² with 12 points per decade. The photocurrent density with 106 to 10⁸ Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The alternating current voltage was 5 mV with 12 points per decade. The alternating current voltage was 5 mV with 12 points per decade. The alternating current voltage was 5 mV with 12 points per decade.

Analytic and Characterization Methods. The pyridine-barbituric acid colorimetry according to the absorbance at 600 nm was used for the determination of total cyanide concentration in a UV–vis spectrophotometer (U-3010, Hitachi Ltd., Japan). The cyanate concentration was determined through ion chromatography using a Metrohm piece of equipment (ICS 1500, Dionex, U.S.A.). An aqueous solution of Na₂CO₃ (4.5 mM) and NaHCO₃ (0.8 mM) was used.

The surface morphology was checked using a Hitachi SU-8020 scanning electron microscope (SEM) instrument (Hitachi Ltd., Japan). X-ray diffraction (XRD) analysis was carried out using an Xpert PRO MPD PC system utilizing Cu Kα radiation at a scan rate (2θ) of 0.5° s⁻¹. X-ray photoelectron spectroscopy (XPS) was measured using a PHI Quantera SXM instrument (ULVAC-PHI, Japan). The binding energies were calibrated with C 1s = 284.8 eV. Electrochemical impedance spectroscopy (EIS) analysis was measured at open circuit voltage with a frequency range from 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade. The photocurrent density with 10⁶ to 10⁻² Hz. The alternating current voltage was 5 mV with 12 points per decade.

Oxidation Performance of Ag Cyanide Complexes in the PEC Process. First, a comparison between the LSV features of CN⁻, Ag⁺, and Ag (CN)₂⁻ was performed and given in Figure 1. It can be seen that Ag⁺ chelation by CN⁻ ions increases the oxidation potential of the Ag⁺ ions by at least 500 mV due to the formation of the complex. Therefore, the Ag (CN)₂⁻ complexes were more difficult to oxidize than the Ag⁺ ions. The effect of the applied bias potential ranging from 0.5 to 1.5 V on the PEC oxidation of Ag cyanide complexes at the prepared g-C₃N₄ electrode was examined. The slight removal of CN⁻ and recovery of silver was confirmed. The oxidation of CN⁻ and silver recovery at 1.0 V was slightly higher than that at 0.5 and 1.5 V (Figure S1 in the Supporting Information). Therefore, the applied bias potential of 1.0 V was selected in the subsequent experiments.

The PEC oxidation of Ag cyanide complexes using the g-C₃N₄ photoanode was performed in the absence and presence of H₂O₂ at 1.0 V bias potential. The g-C₃N₄ photoanode was repeatedly utilized for seven times with the same bias potential. As shown in Figure 2a, both the oxidation efficiency of CN⁻ and the recovery ratio of Ag increase with the recycling times. In the first and second case, only a slight removal of CN⁻ is observed. The recovery ratio of Ag, which is defined as (initial amount of Ag − residual amount of Ag)/initial amount of Ag, is lower than 20%. In the third case, an obvious increase in CN⁻ removal efficiency and Ag recovery ratio is observed, which are determined to be 35.9% and 41.3%, respectively. In the fifth and seventh case, the removal efficiency of CN⁻ is only slightly increased. By contrast, the Ag recovery ratio is largely increased to be 72% and 92%, respectively.

In the presence of 20 mM H₂O₂, as shown in Figure 2b, the CN⁻ removal and Ag recovery are enhanced in contrast to those without H₂O₂, which also increase with the recycling times. The removal of CN⁻ notably increases from 37.7% to 60.2%, 70.3%, 70.7%, and 74.1%, respectively, and the recovery of Ag increases from 23.0% to 55.2%, 69.3%, 71.4%, and 87.7%, respectively. The removal of Ag (CN)₂⁻ can be higher than 60% when the g-C₃N₄ photoanode was used twice or many times as well as the Ag recovery.

Mass Balance of Silver and Nitrogen in PEC Processes. Figure 3 shows the distribution of Ag species with recycling times.
in the g-C3N4 PEC process in the absence or presence of H2O2 addition after 150 min of reaction. As shown in Figure 3a, the percentage of Ag (by wt %) deposited onto the anode, cathode, and in the solution are 0.7%, 23.7%, and 75.5% for the first time, respectively. With the increase of recycling times, the Ag amount deposited onto the anode and cathode increases largely.

With the addition of H2O2, as shown in Figure 3b, the percentages of Ag (by wt %) deposited onto the anode, cathode, and in the solution are 5.2%, 24.2%, and 70.5% for the first time, respectively. With the increase of repetition times, the deposited Ag amount onto the anode and cathode decreases and tends to be stable. At the seventh time, the deposited Ag amounts onto the anode and the cathode are determined to be 59.5% and 14.1%, respectively. It is clear that the Ag deposition onto the anode increases with the recycling times and facilitates the PEC oxidation of Ag-cyanides. Moreover, the addition of H2O2 increases the Ag deposition rate on both anode and cathode as well as the deposition amount.

Surface Variation of the g-C3N4 Photoanode for Various Reaction Times. Figure 4 showed the SEM surface micrographs of the virgin g-C3N4 photoanode (Figure 4a) and g-C3N4 photoanode used in the PEC process for various times (Figure 4b–f). As shown in Figure 4a,b, after PEC oxidation reaction for one time, the surface of the g-C3N4 photoanode is similar to that of the virgin g-C3N4 photoanode. As shown in Figure 4c–f, some particles can be seen on the surface of the g-C3N4 photoanode, linking together with g-C3N4 particles. For the seventh time, the g-C3N4 photoanode surface is nearly fully covered by crystal particles.

The XRD patterns of the g-C3N4 photoanode for different recycling times are shown in Figure 5a. As depicted in Figure 5a, the peaks centered at 27.3° were indexed to the (002) diffractions of g-C3N4.27,28 This peak can still be observed after seven times of PEC process. By contrast, the peak at 13.2° for g-C3N4 is negligible. Four peaks at 30.2°, 35.1°, 51.0°, and 60.5° are observed, which can be assigned to the (222), (400), (441), and (700) planes of ITO substrates, respectively. The peaks at 30.2° (110), 32.0° (200), 32.2° (−111), 34.1° (022), 37.1° (111), 39.3° (202), 53.8° (−311), 56.5° (−113), 62.4° (−221), and 66.9° (400), all indexed as diffractions of AgO, can be observed after various recycling times of the PEC process. It is clear that AgO particles were deposited on the g-C3N4 photoanode. The intensity of these peaks increases with the increase of recycling times, which indicated the increased amount of deposited AgO particles.

The Ag 3d and Ag MNN XPS spectra of g-C3N4 for different times of the PEC process are shown in Figure 5b,c. The Ag 3d XPS spectra of g-C3N4 at different times, which are separated into two peaks centered at 37.0° and 37.4°, correspond to AgO. The two peaks in Auger electron spectroscopy of Ag centered at 35.5° and 350.5 eV are also ascribed to AgO. These results confirmed the generation of AgO species onto the g-C3N4 film electrode.

Surface Variation Analysis of the Titanium Cathode. Figure 6a–e shows the SEM micrographs of the titanium cathode.
for different recycling times in the PEC process. As observed in Figure 6a,b, the titanium electrode after two PEC processes of Ag cyanide degradation showed a flocculent structure, probably corresponding to silver nanowires. As shown in Figure 6c–e, granular sediments of Ag can be observed on the titanium electrode surface with a structure of blocks. Moreover, the deposition amount and deposition size of Ag both increase with the repetition and almost cover the titanium electrode surface after seven times of the PEC process. Figure 6f,g showed the EDS image of the titanium electrode after seven times of the PEC process.

Figure 4. SEM images of the g-C₃N₄ photoanode with various recycling times of the PEC process: (a) g-C₃N₄ before the reaction; (b) 1st; (c) 2nd; (d) 3rd; (e) 5th; (f) 7th.

The surface elemental composition and the valence states of elements on titanium for various times in the PEC process were furthermore investigated by XPS. As shown in Figure 7a, there are C, N, O, and Ag signals in the survey spectrum of the g-C₃N₄ film surface. Figure 7b,c show the Ag 3d and Ag MNN XPS spectra of the titanium cathode in the PEC process for different times. The Ag 3d XPS spectra of the titanium cathode at different times, which were separated into two peaks centered at 367.8 and 373.8 eV, correspond to Ag with zero value. And the two peaks in Auger electron spectroscopy of Ag at 358.2 and 352.2 eV can also be attributed to Ag⁰. Therefore, it is concluded that the deposited particles onto the cathode was metal Ag.

A Proposed Reaction Mechanism. Figure 8 shows the photocurrent response of the g-C₃N₄ photoanode used for various times under visible light irradiation in the absence and presence of H₂O₂. The photocurrent density of the g-C₃N₄ photoanode increases with the increase of recycling times (Figure 8a). It is clear that the g-C₃N₄ photoanode after the PEC oxidation process exhibits a much higher photocurrent response than that of the original g-C₃N₄ photoanode. In addition, the dark current also increases. It is proposed that the deposition of AgO species enhanced the photocurrent response and the electrical conductivity of the g-C₃N₄ photoanode. In the case of
H₂O₂ addition, as shown in Figure 8b, the photocurrent and dark current of the g-C₃N₄ photoanode increase more remarkably and quickly with the repetitive use of the g-C₃N₄ photoanode.

EIS spectra of the g-C₃N₄ photoanode are shown in Figure S2 of the Supporting Information. The arc radius of the g-C₃N₄ photoanode decreases with the reaction times in both the absence and presence of H₂O₂ addition. Clearly, the deposition of AgO leads to a significantly decreased diameter of the semicircular Nyquist plot as compared to virgin g-C₃N₄ photoanode in both g-C₃N₄ and g-C₃N₄/H₂O₂ PEC processes, suggesting a faster charge transfer rate and more quick separation of the photogenerated electron–hole pairs.2⁷

The main reactive species involved in PEC systems were first checked by the ESR technique, using BMPO as the radical scavenger. As shown in Figure 9a,b, the BMPO/•O₂⁻ signal and BMPO/•OH signal are both detected in the g-C₃N₄ PEC system and the g-C₃N₄/H₂O₂ PEC system with g-C₃N₄ deposited by AgO after the seventh repetition. Moreover, the BMPO/•OH signal in the g-C₃N₄/H₂O₂ PEC system was stronger than that in the g-C₃N₄ PEC system.

Furthermore, in order to investigate the role of reactive oxidative species, trapping experiments were also performed. Herein, ethanol was used as the •OH scavenger, and N₂ aeration was used to inhibit the formation of •O₂⁻ radicals. As shown in Figure S3a,b, after the addition of ethanol, the removal of cyanide is decreased from 46.93% to 16.33% in the g-C₃N₄ PEC system and from 74.16% to 23.42% in the g-C₃N₄/H₂O₂ PEC system, respectively. After purging with N₂, the removal of cyanide is decreased from 46.93% to 8.14% in the g-C₃N₄ PEC system and from 74.16% to 23.42% in the g-C₃N₄/H₂O₂ PEC system, respectively. It is clear that the inhibition of N₂ purging is more significant with respect to ethanol in the g-C₃N₄ PEC system, indicating •O₂⁻ itself could contribute to the oxidation. By contrast, the inhibition caused by ethanol addition is more significant than N₂ purging in the g-C₃N₄/H₂O₂ PEC system, indicating the •OH was not only formed by the in situ generated H₂O₂ from •O₂⁻ reduction, but also resulted from the added H₂O₂.

Based on the above results and analysis, a possible mechanism for the H₂O₂ enhanced PEC oxidation by the g-C₃N₄ photoanode with Ag deposition is proposed. Under visible light irradiation, the photogenerated electron–hole pairs were generated from the g-C₃N₄ photoanode with photon energy equal to or greater than approximately 2.68 eV. With the repeated use of the g-C₃N₄ photoanode, the deposition of AgO onto the photoanode as a semiconductor improved its electrical conductivity.2⁹ Thus, the photogenerated electrons from g-C₃N₄ can more easily transfer to the titanium counter electrode and be captured by O₂, generating •O₂⁻ and •OH radicals, which were responsible for the oxidation of Ag(CN)₂⁻ into CNO⁻. And Ag⁺ ions can be oxidized into AgO on the g-C₃N₄ photoanode or reduced to metal Ag onto the cathode.3⁰ The generated •O₂⁻ can react with ••− and produce ••OH radicals to destroy Ag(CN)₂⁻, which was favored by the deposited AgO on the photoanode in the PEC process, as confirmed by ESR spectroscopy (Figure S4). Furthermore, H₂O₂ afforded the additional production of ••OH by the reaction with ••−. Thus, the removal of cyanide was enhanced. The above process was also expressed in eqs 1–8.

\[
\text{AgO/g-C₃N₄} + hν → e^- + h^+
\]  
\[
e^- + O_2 → •O₂⁻
\]  
\[
•O₂⁻ + 2H^+ + e^- → H₂O₂
\]  
\[
H₂O₂ + e^- → •OH + OH^-
\]  
\[
•O₂⁻ + 2H^+ + 2e^- → •OH + OH^-
\]  
\[
\text{Ag(CN)₂}^- + 4•OH → Ag^+ + 2CNO^- + 2H₂O
\]  
\[
\text{Ag(CN)₂}^- + •O₂⁻ → Ag^+ + 2CNO^- 
\]  
\[
Ag^+ + 2OH^- + hν → AgO + e^- + H₂O
\]
CONCLUSIONS

The g-C₃N₄ film was synthesized onto ITO substrate by a calcination method and used as a photoanode to destroy Ag cyanide complexes and recover silver by a PEC process. The PEC process was enhanced with the addition of H₂O₂. With the repeated use of the g-C₃N₄ photoanode, the oxidation of Ag cyanide complexes and simultaneous Ag recovery were enhanced. The Ag species deposited onto the photoanode and cathode were AgO and Ag⁰ respectively. AgO deposition increased the electrical conductivity of the g-C₃N₄ photoanode and promoted the separation of electron−hole. •O₂⁻ and •OH were demonstrated to be the main active radicals for oxidizing Ag (CN)₂⁻ into CNO⁻ in PEC systems, and the accelerated photogenerated electrons to the cathode can be captured by O₂ or H₂O₂, generating more •O₂⁻ and •OH radicals, which facilitated the destruction of cyanide as well as the Ag recovery.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b00395.

Effect of applied potentials on the CN⁻ removal and silver recovery, EIS spectra of the g-C₃N₄ photoanode, influence
of scavengers on PEC processes, and ESR spectroscopy of BMPO–$O_2^-$ adducts in the g-C3N4 PEC process and g-C3N4-7th PEC process (PDF)

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**Notes**

The authors declare no competing financial interest.

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