Enhanced Photoelectrocatalytic Decomposition of Copper Cyanide Complexes and Simultaneous Recovery of Copper with a Bi_2MoO_6 Electrode under Visible Light by $\text{EDTA}/\text{K}_4\text{P}_2\text{O}_7$

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S Supporting Information

ABSTRACT: Simultaneous photoelectrocatalytic (PEC) oxidation of cyanides and recovery of copper in a PEC reactor with a Bi_2MoO_6 photoanode was investigated at alkaline conditions under visible light irradiation. The surface variation of the Bi_2MoO_6 photoanode and titanium cathode was characterized. The Cu mass distribution onto the anode, in the solution, and onto the cathode was fully investigated. In the individual PEC oxidation of copper cyanides, the formation of a black copper oxide on the anode occurred. By keeping the initial cyanide concentration at 0.01 mM, the effect of $\text{EDTA}/\text{K}_4\text{P}_2\text{O}_7$ was examined at different molar ratios of $\text{EDTA}/\text{K}_4\text{P}_2\text{O}_7$ to cyanide. It was indicated that the oxidation of cyanides increased and simultaneous copper electrodeposition with zero value onto the cathode was feasible at pH 11. Under the optimal conditions, the total cyanide concentration was lowered from 250 to 5.0 mg/L, and the Cu recovery efficiency deposited onto the cathode was higher than 90%. Cyanate was the only product. The role of the photogenerated hole in the oxidation of cyanide ions was confirmed.

INTRODUCTION

Cyanides are widely used in electroplating, mining, and photographic processes due to their unique properties for complexing metals such as copper, silver, gold, or zinc. As a consequence, wastewaters coming out from these activities usually contain large amounts of metal–cyanide complexes.¹ Therefore, it is important to treat the effluents containing these cyanocomplexes previously to their discharge into the environment.

Various treatment procedures, such as adsorption, complexation, and oxidation are known for treating cyanides.^{2,3} The adsorption and complexation processes give highly concentrated products in which toxic cyanides still exist. Ozone or peroxide oxidation does not achieve the complete removal of metal cyanide complexes. The most common method to treat cyanide is alkaline chlorination. However, improper chlorination of cyanide would give evolution of toxic cyanogen chlorides. Ferrate, as a green chemical oxidant, can address some of the concerns of chlorination in the treatment of cyanides.⁴ However, iron cyanide complexes are still needed to be treated carefully.

The electrochemical oxidation of cyanide and copper cyanides has been largely investigated.^{5,6} The results indicated that rapid oxidation of cyanide to cyanate was observed with the formation of a black copper oxide film at the anode. It was recognized that the copper oxide film is found to be catalytic, capable of electro-oxidizing hydroxide to oxygen and cyanate to

nitrate.⁷ However, the overdose copper oxide film will limit the oxidation reaction of cyanide or copper cyanide. In the meantime, the Cu recovery onto a cathode with a zero value was desired. Thus, it was desired to oxidize the cyanide and recover the liberated Cu ions with zero value simultaneously. Organic ligands such as EDTA or $\text{K}_4\text{P}_2\text{O}_7$ form strong complexes with heavy metal ions and are commonly used in industrial cyanide plating processes. Their effect on the cyanide oxidation was little studied.

Photocatalytic oxidation of cyanide was also extensively investigated. When using TiO_2 in the slurry form or deposited on a support, the removal of cyanides was shown to be possible.^{8–11} In most cases, cyanate is found to be the oxidation product, which could be further oxidized simultaneously on the surface of TiO_2 to produce nitrate and carbonate. The photocatalytic oxidation of cyanide in aqueous TiO_2 suspensions with and without EDTA present in the reaction mixture was investigated by Osathaphan et al.¹² The results indicated that the presence of EDTA reduces the photocatalytic oxidation rate of cyanide due to occupancy of the active sites. Unfortunately, TiO_2 when applied as a suspension or slurry has to be filtered, making this approach uneconomical and

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preventing the industrial application of this process for the cyanides elimination.

To achieve an effective treatment of copper cyanides, not only the oxidation of the cyanide (CN^-) groups but also the recovery of metal would also be desirable in order to accomplish a double objective: to avoid cyanide and metal pollution and to reuse copper in new processes. Recently, combined electro-oxidation and photocatalysis using a semiconductor film electrode has shown great potential for destruction of organic contaminants and bacterial inactivation, combined with individual electro-oxidation and photocatalysis.^{13–15} In our previous work, the TiO_2 film electrode was used as the anode and photoelectrocatalytic (PEC) treatment of Cu-EDTA complexes with the simultaneous recovery of Cu onto the stainless cathode was achieved at neutral conditions.¹⁶ Generally, the copper cyanides exhibited different behavior with Cu-EDTA complexes. It was known that oxidation of cyanide should be in the pH value higher than 10.0 in order to avoid the generation of HCN toxic gas. Thus, the hydrolysis and precipitation of the liberated metal ions occur easily, which will inhibit the metal ion deposition onto the cathode. Recently, bibased ternary oxide photocatalysts responsive to visible light have shown great potential in applications such as splitting water, solar cells, and environmental purification.^{17–19} In our previous work, the Bi_2MoO_6 film photoanode was prepared and exhibited high PEC activities toward the degradation of organic dyes under visible light irradiation.²⁰

Herein, the PEC degradation of copper cyanides using the Bi_2MoO_6 photoanode in the absence and presence of EDTA or $\text{K}_4\text{P}_2\text{O}_7$ was investigated under visible light irradiation. The results indicated that the copper oxide deposition on the anode with the simultaneous cyanide destruction without EDTA or $\text{K}_4\text{P}_2\text{O}_7$, led to the inhibition of PEC decomposition of CN^- ions using Bi_2MoO_6 photoanode under visible light irradiation. In the presence of EDTA or $\text{K}_4\text{P}_2\text{O}_7$, copper cyanides were efficiently destroyed, and copper was efficiently recovered by electrochemical reduction deposition at the cathode. The enhanced mechanism was also proposed.

EXPERIMENTAL SECTION

Photoelectrochemical Experiments. Degradation experiments were performed in a rectangular ($50 \times 50 \times 100 \text{ mm}^3$) reactor made of quartz glass. The reactor, which contained a 70 mL sample solution, allowing 6 cm of the supported film electrode to be immersed into the solution, was placed 3 cm in front of a 150 W Xe lamp purchased from the German Osram. A UV cutoff filter ($\lambda > 420 \text{ nm}$) filter purchased from Shanghai Seagull Colored Optical Glass Co., Ltd. was used to remove light with wavelengths below 420 nm. The PEC reaction employed a basic electrochemical system (CHI 660b, Shanghai Chenhua Instruments Co., Ltd.) connected with a working electrode (the Bi_2MoO_6 film deposited onto the ITO electrode, active area of 25 cm^2), a counter-electrode (titanium plate with the same active area), and a reference electrode (a saturated calomel electrode (SCE)). The Bi_2MoO_6 film deposited onto the ITO electrode was prepared according to the procedure described in our previous work.²⁰ The ratio of $[\text{CN}^-]:[\text{Cu}]$ remained much higher than four in the experiment, and it is therefore likely that the predominant species was $\text{Cu}(\text{CN})_3^{2-}$ according to our previous analysis of cuprous cyanide species distribution with the program Visual MINTEO 3.0.²¹

Analytical Methods. All experiments were performed in duplicate, and the analysis of each parameter was done in

triplicate for each run. The total cyanide concentration (free cyanide plus weak acid dissociable cyanocomplexes) was determined through a standard colorimetric method using a pyridine-barbituric acid reagent to form a highly colored complex with a maximum absorbance at 575 nm.²² The detection limit of determining total cyanide concentration was 0.0045 mg/L. Free cyanide concentration was potentiometrically determined by using a CN^- -selective electrode in an expandable ion analyzer (Orion 720A). UV-vis analysis was performed using an UV-vis spectrophotometer (U-3010, HITACHI). The detection limit of determining cyanide concentration was 0.5000 mg/L. pH values were measured using a pH meter (310P-02, Thermo Fisher, U.S.A.).

The Bi_2MoO_6 film anode and titanium cathode under various processes were analyzed by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and scanning electron microscopy (SEM)-energy dispersive X-ray (EDX). Prior to the measurement, the electrode was washed with water to remove electrolyte. XPS analysis was obtained using a PHI Quantera SXM (PHI-5300/ESCA, ULVAC-PHI, INC). SEM micrographs were obtained by using JEOL JSM-6301 equipment with electron beam energy of 20 keV. XRD was recorded on a Scintag-XDS-2000 diffractometer with Cu $K\alpha$ radiation. The concentration of copper ions in the reaction solution under various conditions was measured using an inductively coupled plasma optical emission spectrometer (OPTIMA 200, Perkin Elmer, U.S.A.).

RESULTS AND DISCUSSION

Photoelectrocatalytic Treatment of Copper Cyanides.

First, the PEC treatment of $\text{Cu}(\text{CN})_3^{2-}$ s under various bias potentials was investigated. Meantime, the recovery ratio of Cu was also given. Herein, the recovery ratio of Cu^{2+} ions is defined as $R_{\text{Cu}}(\%)$ shown in the following equations.

$$R_{\text{Cu}}(\%) = 100 \times \frac{(\text{init. Cu} - \text{remain. Cu}) \text{ in react. cell}}{\text{init. Cu in react. cell}}$$

where “init. Cu” is the initial amount of Cu ions; “remain. cell” is the remaining amount of Cu ions; “in react. cell” is in the reaction cell; and “init. Cu in react. cell” is the initial amount of Cu ions in the reaction cell.

As shown in Figure 1, a slight removal of total cyanide is observed in the individual photocatalysis process, and nearly no Cu recovery is observed. With the applied bias potential of 1.0

Figure 1. Concentration variation of total cyanide and recovery ratio of copper in the photocatalysis and photoelectrocatalytic oxidation with various potentials ($[\text{Cu}(\text{CN})_3^{2-}] = 0.5 \text{ mM}$; $\text{pH} = 11$).

V, nearly no change is observed. By contrast, an obvious increase of total cyanide removal and the recovery ratio of Cu are observed with the applied bias potentials of 1.5, 2.0, and 2.5 V (vs SCE). Among them, the total cyanide removal and the Cu recovery achieve the largest value at the bias potential of 2.0 V, which are determined to be 68.4% and 64.1% at 120 min, respectively.

In the meantime, the conversion byproducts of CN^- ions were investigated. As shown in Figure 2, the intermediate of

Figure 2. Generated intermediates and N mass balance in the photoelectrocatalytic oxidation of $\text{Cu}(\text{CN})_3^{2-}$ at 2.0 V bias potential ($[\text{Cu}(\text{CN})_3^{2-}] = 0.5 \text{ mM}$; $\text{pH} = 11$).

cyanate (CNO^-) is identified, and its concentration increases with the decrease of total cyanide concentration. It has been recognized that cyanide ion was believed to react with O_3 , $\cdot\text{OH}$ and H_2O_2 , yielding intermediate compounds (OCN^- , NO_2^- , $\text{HO}-\text{C}=\text{N}$, $\text{O}=\text{C}-\text{NH}_2$, $\cdot\text{OOC}(\text{O})\text{NH}_2$) and final byproducts (NO_3^- , NO_2^- , NH_4^+ , N_2 , HCO_3^- , CO_3^{2-} , saponified compounds).²³ The byproducts observed in solution during the photocatalytic degradation of cyanide were identified as cyanates and nitrites.²⁴ Herein, no intermediates such as NH_4^+ and NO_3^- are identified in the process. The almost stoichiometric nitrogen balance, given by the N-containing products of the reaction is also noted.

Photoelectrocatalytic Treatment of Copper Cyanides in the Presence of EDTA. The above results indicated that the efficiencies of total cyanide removal and Cu recovery in the PEC process were desired to be increased. It was known that EDTA used as chelant usually coexisted with the cyanide pollutants. Therefore, the total cyanide removal and Cu recovery with the addition of various EDTA amounts were investigated under the bias potential of 2.0 V with the same initial concentration of $\text{Cu}(\text{CN})_3^{2-}$. As shown in Figure 3(a), with the increase of ratio of $[\text{EDTA}]$ to $[\text{CN}^-]$, the efficiencies of total cyanide removal and Cu recoveries increase obviously. At the $[\text{EDTA}]/[\text{CN}^-]$ ratio of 5:1, the removal efficiency of the total cyanide is determined to be 99.8%, and the Cu recovery ratio is 91.0% at 120 min. It is clear that the addition of EDTA largely increases the efficiencies of cyanide oxidation and Cu recovery. With respect to the intermediates, it is interesting to observe from Figure 3(b) that the amount of CNO^- decreases with the increase of NH_4^+ when the ratio of $[\text{EDTA}]$ to $[\text{CN}^-]$ increases. The NH_4^+ ions were generated from the PEC oxidation of EDTA, as indicated in our previous results.¹⁶ Simultaneously, total organic carbon (TOC) variation in the reaction processes with various ratios of $[\text{EDTA}]/[\text{CN}^-]$ were analyzed. The results indicated that nearly no TOC decrease in the reaction process (Supporting Information,

Figure 3. (a) The total cyanide removal and copper recovery; (b) generation of CNO^- and NH_4^+ ; and (c) the copper mass balance in the photoelectrocatalytic process with various ratios of $[\text{EDTA}]$ to $[\text{CN}^-]$ ($[\text{Cu}(\text{CN})_3^{2-}] = 0.5 \text{ mM}$; $\text{pH} = 11$; 2.0 V bias potentials).

Figure SI-1). In one way, EDTA was destroyed into small molecular acids; in another way, destruction of EDTA with high concentration was limited.

Furthermore, the distribution of Cu species was analyzed at various EDTA amounts. As shown in Figure 3(c), without the EDTA addition, the percentages of Cu (by wt %) deposited onto the anode, in the solution, and deposited onto the cathode are 31.3%, 37.7%, and 31.0%, respectively. With the increase of EDTA amount, the Cu amount deposited onto the anode and in the solution decrease and the Cu amount deposited onto the cathode increase gradually. At the $[\text{EDTA}]$ to $[\text{CN}^-]$ ratio of 5:1, the Cu mass percentage deposited onto the anode and the cathode are determined to be 10.7% and 86.6%, respectively. Thus, it is obvious that the addition of EDTA to the solution increases the Cu amount deposited onto the cathode. The Cu deposition onto the anode is inhibited, which is favorable to the

PEC oxidation of Cu-cyanides. The enhanced process will subsequently be discussed.

Photoelectrocatalytic Treatment of Copper Cyanides in the Presence of $K_4P_2O_7$. Generally, $K_4P_2O_7$ coexisted with the cyanide in the electroplating wastewater. Therefore, the effect of $K_4P_2O_7$ on the total cyanide removal and copper recovery in the PEC degradation of $Cu(CN)_3^{2-}$ was investigated at the 2.0 V bias potential with the same initial concentration of $Cu(CN)_3^{2-}$ (Figure 4(a)). The intermediates and Cu mass distribution are also given in Figure 4, parts (b) and (c), respectively.

It can be seen from Figure 4(a) that the efficiencies of total cyanide removal and Cu recovery increase with the amount of $K_4P_2O_7$. With respect to the intermediates, the intermediate of CNO^- increase with the increased amount of $K_4P_2O_7$; nearly no NH_4^+ generation is observed (Figure 4(b)). With respect to the Cu mass distribution, it is observed from Figure 4(c) that

Figure 4. (a) Effect of $K_4P_2O_7$ on total cyanide removal and copper recovery; (b) effect of $K_4P_2O_7$ on the concentration variation of CNO^- and NH_4^+ ; and (c) the copper mass balance in the photoelectrocatalytic process with various concentration of $K_4P_2O_7$ ($[Cu(CN)_3^{2-}] = 0.5$ mM; pH = 11; 2.0 V bias potential).

the addition of $K_4P_2O_7$ not only leads to the efficient removal of Cu from the solution, but also increases the deposited amount of Cu onto the cathode. The enhanced mechanism will also be subsequently discussed.

Involved Active Species. The photocatalytic oxidation of cyanide over TiO_2 particles has been reported to occur via both direct electron transfer to the holes and homogeneous hydroxyl radicals attack in the bulk solution.^{8,9} Tertiary butanol (t -BuOH) which is known as $\cdot OH$ radicals scavengers, were used to test the role of $\cdot OH$ radicals. As shown in Figure 5(a), the efficiencies of total cyanide removal and Cu recovery remain nearly constant with the addition of various t -BuOH concentrations in the presence of $K_4P_2O_7$. Nearly no effect of t -BuOH addition on the generation of intermediates and Cu mass distribution is observed in Figure 5, parts (b) and (c), respectively. Therefore, it was concluded that the role of active

Figure 5. (a) The removal of total cyanide and copper recovery in the PEC process of $Cu(CN)_3^{2-}$; (b) concentration variation of CNO^- and NH_4^+ ; and (c) the copper mass balance in the photoelectrocatalytic process of $Cu(CN)_3^{2-}$ with various $C_4H_{10}O$ concentration ($[Cu(CN)_3^{2-}] = 0.5$ mM; pH = 11; $[K_4P_2O_7] = 5$ mM; 2.0 V bias potential; 120 min).

$\cdot\text{OH}$ radicals in the decomposition of total cyanide can be ignored. Maybe the photogenerated hole was responsible for the total cyanide decomposition.²⁵ It was reported that cyanide is oxidized by photogenerated $h\nu^+$ to form $\text{CN}^\bullet$ radicals. The dimerization of $\text{CN}^\bullet$ forms cyanogen, which subsequently hydrolyzes to result in cyanate and cyanide ions.¹²

The effect of aeration on the PEC treatment of $\text{Cu}(\text{CN})_3^{2-}$ was furthermore investigated. It can be seen from Figure 6(a)

Figure 6. Effect of N_2 and O_2 sparged electrolyte in the photoelectrocatalytic process: (a) The removal of total cyanide and copper recovery ratio; (b) the generation of cyanate and NH_4^+ ; and (c) the copper distribution ($[\text{Cu}(\text{CN})_3^{2-}] = 0.5 \text{ mmol/L}$; $[\text{Na}_2\text{SO}_4] = 1.0 \text{ mmol/L}$; $[\text{NaOH}] = 1.0 \text{ g/L}$; $\text{pH} = 11.0$).

that the removal efficiency of the total cyanide in the presence of O_2 is higher than in the presence of N_2 and blank conditions; a similar trend is observed with the Cu recovery. Meantime, more cyanide is transferred into the CNO^- in the presence of more dissolved O_2 (Figure 6 (b)). It is proposed that O_2 supports the oxidation of the liberated $\text{Cu}^+/\text{Cu}^{2+}$ ions and acts as reagent in the oxidation of released cyanide to cyanate species. The Cu mass distributions in the various processes

were also investigated. As shown in Figure 6(c), most of the Cu is deposited onto the anode with the Cu oxides species in the presence of O_2 . By contrast, the amount of Cu deposited onto the cathode is increased in the presence of N_2 . In the PEC oxidation of $\text{Cu}(\text{CN})_3^{2-}$, the oxidation of $\text{Cu}^+/\text{Cu}^{2+}$ ions in the presence of more dissolved O_2 is enhanced, leading to the more deposition of Cu oxides onto the Bi_2MoO_6 film anode.

Analysis of the Surface Variation of the Electrodes.

The surface variation of the Bi_2MoO_6 film anode and titanium cathode under various processes was characterized by SEM-EDX, XRD, and XPS analysis. In comparison with that in the absence of $\text{Cu}(\text{CN})_3^{2-}$ (Figure 7(a)), it can be seen from Figure 7(b) and Figure SI-2(a) that the Bi_2MoO_6 film anode and the cathode was covered by a layer of copper oxides in the PEC treatment of $\text{Cu}(\text{CN})_3^{2-}$. By contrast, as shown in Figure 7(c), Figure SI-2(b) Figure 7(d), and Figure SI-2(c), the formation of copper oxides film on the anode was efficiently inhibited in the presence of EDTA or $\text{K}_4\text{P}_2\text{O}_7$, respectively. And, the liberated Cu ions were efficiently deposited onto the cathode, respectively.

The chemical nature of the surface layers deposited onto the anode and cathode was further investigated by XPS analysis and XRD analysis. For the chemical identification of the copper surface species, analysis of both Cu 2p and Cu LMM Auger lines was performed. It can be seen from Figure 8, parts (a) and (b), that the Cu appears on the Bi_2MoO_6 film anode and the titanium cathode in the presence of $\text{Cu}(\text{CN})_3^{2-}$. By contrast, the peak intensity of Cu decreases at the anode with the increase of the Cu amount at the cathode in the presence of EDTA and $\text{K}_4\text{P}_2\text{O}_7$. Particularly, the peak intensity of Cu on the anode nearly disappears in the presence of $\text{K}_4\text{P}_2\text{O}_7$. The SEM-EDX and XPS results furthermore confirmed the results shown in Figure 3(c) and 4(c) on the Cu mass distribution at the anode, in the solution, and at the cathode.

For the chemical identification of the copper surface species, XPS spectra in the Cu 2p $_{3/2}$ region for the Bi_2MoO_6 film anode and titanium cathode under various conditions are given in Figure 8, parts (c) and (d), respectively. The presence of Cu^{2+} is characterized with the specific binding energies of $934.5 \pm 0.3 \text{ eV}$ in the presence of $\text{Cu}(\text{CN})_3^{2-}$ complexes after the PEC reaction for 120 min, which confirms the formation of Cu oxides in the PEC process (Figure 8(c)). By contrast, the peak at the binding energies of $932.5 \pm 0.3 \text{ eV}$ appear in the presence of EDTA, which indicates the presence of Cu^{1+} on the anode.²⁶ Particularly, no peak was observed for Cu in the presence of $\text{K}_4\text{P}_2\text{O}_7$. In the case of titanium cathode (Figure 8 (d)), the peaks at binding energies of 935 and 937 eV confirm the presence of Cu^{2+} and $\text{Cu}^{1+}/\text{Cu}^0$, respectively. The Cu^{2+} and Cu^{1+} will be electrochemically reduced to Cu^0 . Combined with the XRD results (shown in Figure SI-3), it was concluded that the addition of EDTA/ $\text{K}_4\text{P}_2\text{O}_7$ efficiently inhibited the deposition of Cu oxides onto the anode and promoted the electrochemical reduction of the liberated Cu ions onto the cathode.

Proposed Reaction Mechanism. The formation of Cu oxides on the anode during the electrochemical oxidation of copper cyanide complex solutions under alkaline conditions has been well recognized, which can be expressed in terms of the following reactions (eqs 1–4).²⁷ Simultaneously, copper electrodeposition occurs on the cathode with the liberation of CN^- ions according to the results.²⁸

Figure 7. SEM analysis of the Bi_2MoO_6 film anode and titanium cathode in the various processes: (a) blank; (b) in the presence of $\text{Cu}(\text{CN})_3^{2-}$; (c) in the presence of EDTA; and (d) in the presence of $\text{K}_4\text{P}_2\text{O}_7$.

The mechanism of photocatalytic oxidation of cyanide using TiO_2 has been documented.^{8–10} The oxidation of cyanide is possible via the reaction of CN^- with surface hydroxyls or holes. According to Domenech and Peral, the initial step of cyanide photocatalytic oxidation is the formation of cyanide radical, which subsequently dimerizes to form cyanogens.¹² Finally, the cyanogens molecule undergoes dismutation under alkali conditions to give cyanide and cyanate. The produced cyanate is further oxidized to give NO_3^- and CO_2 . The corresponding reactions are presented as follows (eqs 5–8):

Therefore, it was concluded that CN^- ions were oxidized into CNO^- by photogenerated holes with the simultaneous oxidation of Cu^+ to Cu^{2+} in the PEC process of $\text{Cu}(\text{CN})_3^{2-}$ at the Bi_2MoO_6 film anode. In the meantime, CuO and CuOOH particles were generated. As a result, the PEC reaction was inhibited. In the presence of EDTA or $\text{K}_4\text{P}_2\text{O}_7$, with the oxidation of CN^- ions into CNO^- , the complexation reaction of liberated $\text{Cu}^+/\text{Cu}^{2+}$ with EDTA or $\text{P}_2\text{O}_7^{4-}$ occurred immediately with oxidation of Cu -EDTA complexes, which were electrochemically reduced at the titanium cathode. A model for a such process can be assumed in a four-step reaction as follows: adsorption of copper cyanide complexes onto the Bi_2MoO_6 surface, followed by oxidation of CN^- with the

Figure 8. XPS analysis of the Bi_2MoO_6 anode and titanium cathode in the various processes: (a) XPS full scan of the Bi_2MoO_6 anode; (b) XPS full scan of the titanium cathode; (c) XPS spectrum in the Cu 2p region of the film for the Bi_2MoO_6 anode; and (d) XPS spectrum in the Cu 2p region of the film for the titanium cathode.

liberation of copper into the solution, complexation of Cu with EDTA or $\text{P}_2\text{O}_7^{4-}$ ions with oxidation of Cu-EDTA complexes, and electrodeposition of copper onto the cathode.

Summarily, the PEC oxidation of copper cyanides with the simultaneous recovery of copper by electrochemical reduction at the cathode was achieved under the strong alkaline conditions in the presence of EDTA or $\text{K}_4\text{P}_2\text{O}_7$. Cu can be furthermore recovered by scraping the deposited Cu from the cathode. Following this strategy, the large-scale continuous degradation of cyanide to below legal emission levels and recovery Cu is feasible.

■ ASSOCIATED CONTENT

Supporting Information

Figure SI-1: The removal ratio of TOC at 60 and 120 min in the photoelectrocatalytic process with various ratios of $[\text{EDTA}]$ to $[\text{CN}^-]$; Figure SI-2: SEM analysis of the Bi_2MoO_6 film anode and titanium cathode in the various processes; and Figure SI-3: XRD analysis of the Bi_2MoO_6 anode and titanium cathode in the various processes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Irwin, R. J.; Van Mouweric, M.; Stevens, L.; Seese, M. D.; Basham, W.; *Environmental Contaminants Encyclopedia: Cyanide*; National Park Service, Water Resources Division: Fort Collins, CO, 1997.
- (2) Guro, M. D.; Bremen, W. M. Kinetics and mechanism of ozonation of free cyanide species in water. *Environ. Sci. Technol.* **1985**, *19*, 804–809.
- (3) Young, C. A. Remediation of Technologies for the Management of Aqueous Cyanide Species. In *Cyanide: Social, Industrial and Economic Aspects* Young, C., Ed.; TMS (The Mineral, Metals, and Materials Society) Press: Warrendale, PA, 2001; 175–194.
- (4) Sharma, V. K.; Burnett, C. R.; Yngard, R. A.; Cabelli, D. E. Iron(VI) and iron(V) oxidation of copper(I) cyanide. *Environ. Sci. Technol.* **2005**, *39*, 3849–3854.
- (5) Szpyrkowicz, L.; Zilio-Grandi, F.; Kaul, S. N.; Rigoni-Stern, S. Electrochemical treatment of copper cyanide wastewaters using stainless steel electrodes. *Water Sci. Technol.* **1998**, *38*, 261–268.
- (6) Szpyrkowicz, L.; Kelsall, G. H.; Souto, R. M.; Ricci, F.; Kaul, S. N. Hydrodynamic effects on the performance of an electrochemical reactor for destruction of copper cyanide. Part 2-reactor kinetics and current efficiencies. *Chem. Eng. J.* **2005**, *60*, 535–543.
- (7) Cheng, S. C.; Gattrell, M.; Guena, T.; MacDougall, B. The electrochemical oxidation of alkaline copper cyanide solutions. *Electrochim. Acta* **2002**, *47*, 3245–3256.
- (8) Marugan, J.; van Grieken, R.; Cassano, A. E.; Alfano, O. M. Intrinsic kinetic modeling with explicit radiation adsorption effects of the photocatalytic oxidation of cyanide with TiO_2 and silica-supported TiO_2 suspensions. *Appl. Catal., B: Environ.* **2008**, *85*, 48–60.
- (9) López-Muñoz, M. J.; Aguado, J.; van Grieken, R.; Javier Marugán, J. Simultaneous photocatalytic reduction of silver and oxidation of cyanide from dicyanoargentate solutions. *Appl. Catal., B: Environ.* **2009**, *86*, 53–62.
- (10) Motegh, M.; van Ommen, J. R.; Appel, P. W.; Kreutzer, M. T. Scale-up study of a multiphase photocatalytic reactor—Degradation of

cyanide in water over TiO_2 . *Environ. Sci. Technol.* **2014**, *48*, 1574–1581.

(11) Bhakta, D.; Shukla, S. S.; Chandrasekharalah, M. S.; Margrave, J. L. A novel photocatalytic method for detoxification of cyanide wastes. *Environ. Sci. Technol.* **1992**, *26*, 625–626.

(12) Osathaphan, K.; Chucherdwatanasak, B.; Rachdawong, P.; Sharma, V. K. Photocatalytic oxidation of cyanide in aqueous titanium dioxide suspensions: effect of ethylenediaminetetraacetate. *Sol. Energy* **2008**, *82*, 1031–1036.

(13) Candal, R. J.; Zeltner, W. A.; Anderson, M. A. Effects of pH and applied potential on photocurrent and oxidation rate of saline solution of formic acid in a photoelectrocatalytic reactor. *Environ. Sci. Technol.* **2000**, *34*, 3443–3451.

(14) Quan, X.; Yang, S. G.; Ruan, X. L.; Zhao, H. M. Preparation of titania nanotubes and their environmental applications as electrode. *Environ. Sci. Technol.* **2005**, *39*, 3770–3775.

(15) Sun, H. W.; Li, G. Y.; Nie, X.; Shi, H. X.; Wong, P. K.; Zhao, H. J.; An, T. C. Systematic approach to in-depth understanding of photoelectrocatalytic bacterial inactivation mechanism by tracking the decomposed building blocks. *Environ. Sci. Technol.* **2014**, *48*, 9412–9419.

(16) Zhao, X.; Guo, L. B.; Zhang, B. F.; Liu, H. J.; Qu, J. H. Photoelectrocatalytic oxidation of Cu-EDTA at the TiO_2 electrode and simultaneous recovery of Cu^{2+} by electrodeposition. *Environ. Sci. Technol.* **2013**, *47*, 4480–4488.

(17) Ding, X.; Zhao, K.; Zhang, L. Z. Enhanced photocatalytic removal of sodium pentachlorophenate with self-doped Bi_2WO_6 under visible light by generating more superoxide ions. *Environ. Sci. Technol.* **2014**, *48*, 5823–5831.

(18) Eisenberg, D.; Ahn, H. S.; Bard, A. J. Enhanced photo-electrochemical water oxidation on bismuth vanadate by electrodeposition of amorphous titanium dioxide. *J. Am. Chem. Soc.* **2014**, *136*, 14011–14014.

(19) Kang, D.; Park, Y.; Hill, J. C.; Chor, K. S. Preparation of Bi-based ternary oxide photoanodes BiVO_4 , Bi_2WO_6 , and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ using dendritic Bi metal electrodes. *J. Phys. Chem. Lett.* **2014**, *5*, 2994–2999.

(20) Zhao, X.; Qu, J. H.; Liu, H. J.; Hu, C. Photoelectrocatalytic degradation of triazine-containing azo dyes at $\gamma\text{-Bi}_2\text{MoO}_6$ film electrode under visible light irradiation. *Environ. Sci. Technol.* **2007**, *41*, 6802–6807.

(21) Chen, F. Y.; Zhao, X.; Liu, H. J.; Qu, J. H. Reaction of $\text{Cu}(\text{CN})_3^{2-}$ with H_2O_2 in water under alkaline conditions: Cyanide oxidation, $\text{Cu}^+/\text{Cu}^{2+}$ catalysis and H_2O_2 decomposition. *Appl. Catal., B: Environ.* **2014**, *158–159*, 85–90.

(22) Clescerl, L. S.; Greenberg, A. E.; Eaton, A. D. *Standard Methods for the Examination of Water and Wastewater*; United Book Press, Inc.: Baltimore, Maryland, United States, 1998.

(23) Monteagudo, J. M.; Rodríguez, L.; Villaseñor, J. Advanced oxidation processes for destruction of cyanide from thermoelectric power station waste waters. *J. Chem. Technol. Biotechnol.* **2004**, *79*, 117–125.

(24) Bozzi, A.; Guasaquillo, I.; Kiwi, J. Accelerated removal of cyanides from industrial effluents by supported TiO_2 photocatalysts. *Appl. Catal., B: Environ.* **2004**, *51*, 203–211.

(25) Barakat, M. A.; Chen, Y. T.; Huang, C. P. Removal of toxic cyanide and Cu(II) ions from water by illuminated TiO_2 catalyst. *Appl. Catal., B: Environ.* **2004**, *53*, 13–20.

(26) Casella, I. G.; Gatta, M. Anodic electrodeposition of copper oxide/hydroxide films by alkaline solutions containing cuprous cyanide ions. *J. Electroanal. Chem.* **2000**, *494*, 12–20.

(27) Katagiri, A.; Inoue, H.; Ogure, N. Cathodic polarization of copper electrode in CuCN-KCN solutions and the current distribution for copper deposition on grooved substrates. *J. Appl. Electrochem.* **1997**, *27*, 529–538.

(28) Dudek, D. A.; Fedkiw, P. S. Electrodeposition of copper from cuprous cyanide electrolyte I. current distribution on a stationary disk. *J. Electroanal. Chem.* **1999**, *474*, 16–30.