Photoelectrocatalytic Oxidation of Cu-cyanides and Cu-EDTA at TiO$_2$ nanotube electrode

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Abstract

Oxidation of Cu-cyanides and Cu-EDTA complexes by a photoelectrocatalytic process was investigated at the TiO$_2$ nanotube matrix electrode. The results indicated that Cu oxides were deposited onto the TiO$_2$ nanotube anode in the individual oxidation of Cu-cyanide complexes with the conversion of CN$^-$ into OCN$^-$. In the case of Cu-EDTA, Cu-EDTA was efficiently oxidized at the TiO$_2$ nanotube anode and liberated Cu$^{2+}$ was deposited onto the cathode with only little amount of Cu oxides deposited onto the TiO$_2$ nanotube anode. The above reactions favored at acid conditions. Furthermore, simultaneous oxidation of Cu-cyanide and Cu-EDTA was performed at the TiO$_2$ nanotube electrode with the various ratios of [EDTA]:[CN$^-$]. The Cu mass distribution in the solution, at the anode, and the cathode were investigated in the reaction process. The results indicated that with the increase of [EDTA]:[CN$^-$] ratio, the amount of Cu deposited onto the anode decreased with an increase of the amount of Cu deposited onto the cathode. Addition of EDTA into the reaction solution efficiently inhibited the formation of Cu-oxides onto the TiO$_2$ anode and promoted the Cu deposition onto the cathode. The above results were furthermore confirmed by the SEM-EDX analysis of the anode and cathode under various processes.

1. Introduction

The presence of free and metal-complex cyanides in industrial wastewaters is an important environmental problem considering the acute toxicity of these species for living organisms. Copper cyanide wastewaters arise from industrial electroplating processes, metal finishing and gold mining [1]. Due to its high toxicity, it is essential to find efficient and cost-effective technologies to reduce cyanide concentrations in industrial effluents. Generally, the cyanide and EDTA co-existed in the wastewater. The treatments generally consist of the chlorination oxidation of cyanide species and the subsequent coagulation and precipitation of metal ions at hydroxides [2,3]. However, they involve the use of volatile toxic oxidants, and the resulting sludge is difficult to be handled.

As an alternative to chemical oxidation, the use of electrochemical oxidation for the destruction of cyanides has been studied since the early 1970s [4–8]. This attractive alternative for the treatment of cyanide allowed for the simultaneous recovery of dissolved metal ions. However, on many electrode materials, the electrochemical oxidation of cyanides is kinetically limited and inhibited by adsorbed species. Hence, to achieve viable destruction rates, research has been directed toward the discovery of electrocatalytic processes for the oxidation of cyanide. Such catalytic effects have been observed when either the anode in the electrochemical cell was previously covered with a copper oxide layer or copper ions were present in the solution. In this later case, formation of copper oxide films was also observed in the anode simultaneous to copper deposition at the cathode of the electrochemical reactor [9].

Recently, photoelectrocatalytic (PEC) behavior of semiconductor photocatalyst under a positive potential and light irradiation has been paid more attention in the environmental field [10–13]. PEC oxidation in which a small positive potential was applied across the photocatalytic anode can enhance the separation efficiency of photogenerated holes and electrons and has proven to be more efficient for the pollutants oxidation than the individual photocatalytic process and [14–17]. This PEC method can efficiently destroy undesirable organic compounds and can be used for disinfection in aqueous phase and remove traces of organic species that were stable and difficult to oxidize by means of conventional water treatment methods [18–22].

One-dimensional highly ordered TiO$_2$ nanotube matrix (TNTs) fabricated by electrochemical anodization have been demonstrated as a promising photoanode for use in photocatalytic water
splitting and solar energy conversion with markedly improved efficiency [23,24,25]. Highly ordered TNTs fabricated by direct anodization of titanium (Ti) offer a much larger surface area and facilitate more efficient electron transport than the randomly oriented TiO2 nanoparticles, and are attracting a high interest in various applications including photocatalysis and photoelectrocatalysis [26,27].

Herein, TNTs were fabricated and used as a photoanode to degrade Cu-cyanide and Cu-EDTA complexes via a photoelectrocatalytic process. High efficiency for decomposition of Cu-cyanide/EDTA complexes and simultaneous recovery of Cu at cathode was exhibited and discussed.

2. Experimental section

2.1. Preparation of TiO2 nanotube electrode

The TNTs electrode was fabricated by anodic oxidation at room temperature. Prior to anodization, the pure metallic Ti foil (10 mm × 20 mm × 0.5 mm in size) was cleaned for 15 min in an ultrasonic bath, in a sequence of cleaning solvents (HNO3: HCl, 1:3), ethanol, acetone and finally DI water for 10 min, respectively, and then dried in air at room temperature. In a typical experiment, the TNTs were fabricated by anodization of metallic Ti foil in an electrolyte including ethylene glycol (98.5 v%) solution with additions of 0.3 wt% NH4F and 1.5 v% DI water. In detail, we first immersed the as-prepared Ti foil in 30 mL of the above fresh electrolyte. Then the metallic Ti foil served as the anode and was subjected to potentiostatic anodization in a two electrode configuration containing a Pt foil served as the anode and was subjected to potentiostatic anodization in a two electrode configuration containing a Pt foil cathode at 60 V for 2 hr. Finally, the anode was taken out of the electrolyte and rinsed immediately with DI water thoroughly and then dried in an oven at room temperature.

2.2. Photoelectrochemical experiments

The TNTs electrode (100 mm × 60 mm × 0.5 mm) was used as an anode with an active area of 60 cm²; the stainless steel plate with the same area was used as cathode. The power was provided by a CHI 660b instrument (CH Instrument Co.). The photoelectrochemical behavior of the prepared TiO2 nanotube array electrode in the absence and presence of copper cyanide complexes and Cu-EDTA.

![Image](image_url)

**Fig. 1.** (a) SEM image of top view and cross sectional view of anodically grown TiO2 nanotube matrix; (b) XRD analysis of the titanium substrate and the prepared TiO2 nanotube electrode (TNTs); (c) UV–vis diffuse reflectance spectra (DRS) analysis of the prepared TiO2 nanotube electrode.
was measured via a linear sweep voltammetry method. The working electrode was the prepared TiO$_2$ nanotube array electrode, platinum wire was the counter electrode and a saturated K/KCl was used as reference electrode. Prior to each measurement, the electrolyte was deaerated by nitrogen gas to avoid the influence of dissolved oxygen.

Experiments of photocatalysis, electrolysis, and the PEC process were performed in a 100 mL, a single compartment cell with a 3.5 cm-diameter quartz tube placed in the center and used as the UV bulb housing. UV irradiation was provided by a 5 W-UV lamp with a main wavelength of 254 nm and the light intensity at the center of the compartment was 1.5 mW/cm$^2$ measured with a UV radiometer (Light and Electric instruments Factory of Beijing Normal University). 1 mM NaClO$_4$ was used as electrolyte solution. The reaction solution (70 mL) was put in the PEC reaction cell, which was mixed by a magnetic stirrer (78-2, Pechang Guohua electric appliance Co., LTD) with a stirring speed of 300 rpm at room temperature. At given time, 1 mL solution sample was taken for the analysis. The Cu-EDTA was prepared with the equal molar concentration of CuSO$_4$ and EDTA. In the case of copper cyanides, the copper was added as CuCN, with an excess of KCN in order to produce Cu(CN)$_2^-$ . The initial reaction solution pH value was set as 11 in order to avoid the generation and volatilization of HCN.

2.3. Analytical method

All experiments were performed in duplicate, and the analysis of each parameter was done in triplicate for each run. 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; Free cyanide concentration was potentiometrically determined by using a CN$^-$-selective electrode in an expandable ion analyzer (Orion 720A) [28]. UV–vis analysis was performed using an UV–vis spectrophotometer (U-3010, HITACHI). pH was measured using a pH meter (310P-02, Thermo Fisher, USA).

Concentration of Cu-EDTA was determined using a high performance liquid chromatography (HPLC) (1260, Agilent Technology) equipped with a C-18 column (Agilent Technology) and two detectors connected in series, namely a diode array detector (Waters 996) and a fluorescence detector (Waters 474). The mobile phase consisted of 75:25 solvent: acetonitrile at a flow rate of 1 mL/min and a column temperature of 25 °C. The solvent was composed of 20 mM ammonium phosphate buffer to pH 2.0. The generated intermediates were measured using an ion chromatography (ICS-2000, Dionex, and U.S.A) with a conductivity detector.

The surface morphology of the TNTs was characterized using an S-4800 field emission scanning electron microscope (SEM, Hitachi, Japan) at an accelerating voltage of 10 KV. The energy dispersive X-ray spectroscopy of the cathode was obtained using a JSM-7401 field emission system (JEOL, Japan). X-ray diffraction (XRD) patterns of the TNTs were recorded at room temperature by a Bruker D8 Advance X-ray diffractometer. The diffuse reflectance absorption spectra (DRS) of the samples were recorded in the range from 250 to 800 nm using a Hitachi U-3010 spectroscope equipped with an integrated sphere attachment, and BaSO$_4$ was used as a reference.

3. Results and discussion

3.1. Characterization of the prepared TNTs electrode

Fig. 1 (a) shows SEM images of the anodically grown TiO$_2$ nanotube via the anodization of Ti foil. The self-organized TiO$_2$ layer consists of a dense matrix of vertically aligned nanotubes with an average tube diameter of 40-60 nm and length of ca. 3.36 μm. The anatase of the prepared TNTs matrix is confirmed by the XRD analysis (Fig. 1b). The UV–vis diffuse reflectance spectrum (DRS) of the prepared TNTs matrix is shown in Fig. 1(c). Clearly, its absorption onset was at approximately 390 nm, which agreed well with the bandgap of bulk anatase (εg = 3.2 eV, corresponding to λ = 387 nm).

It can be seen from Fig. 2(a) the current increases with the concentration of copper cyanides at the potential higher than 0.5 V without light irradiation, which indicates that the anodic oxidation of copper cyanides complexes begins at the potential of 0.5 V vs K/KCl. By contrast, the current densities are efficiently increased with the concentration increase of the copper cyanides complexes at low potentials under light irradiation (Fig. 2(b)). This result indicated that photoelectrochemical oxidation of copper cyanides complexes occurred at the TiO$_2$ nanotube array electrode under UV light irradiation. As shown in Fig. 3(a) and (b), similar variation trend of the PEC behavior of the TiO$_2$ nanotube electrode is observed with the increase of Cu-EDTA, which indicates that Cu-EDTA is efficiently oxidized in the PEC process.

![Fig. 2](image-url)
increases at the discussed various increased R 3.2.

Furthermore, cyanides removal = Cu2+ ions was increased by the potential gradient. The holes were driven to the catalyst surface and electrons were driven towards the interior of semiconductor, where they can be swept to the counter electrode. The holes can react with the OH− radicals adsorbed onto the catalyst surface, leading to the generation of active OH•.

3.2. Individual oxidation of Cu-cyanide complexes

Firstly, PEC oxidation of Cu-cyanide complexes was performed at various applied bias potentials. It can be seen from Fig. 4(a) that a slight removal of the total cyanide is observed at the applied bias potential of 0 V. By contrast, total cyanide removal is largely increased at the applied bias potential of 0.5 V. Meantime, it increases with the applied bias potential. At 2.5 V, the total cyanide is nearly removed completely. Recovery of Cu is also observed and the recovery efficiencies increase with the bias potential. Herein, the recovery percentage of Cu2+ ions is defined as RCu(%) shown in the following equations.

\[ RCu(\%) = 100 \times \left( \frac{\text{Initial amount of Cu ions} - \text{remained amount of Cu ions}}{\text{Initial amount of Cu ions}} \right) \text{in the reaction cell} \]

As shown in Fig. 5, intermediates of OCN− are observed. The generated amounts of OCN− increase with the applied bias potential. No generated NH4+− N is observed at the current conditions.

The electrochemical oxidation of cuprocyanide complexes was largely investigated. The results reported by Szpyrkowicz et al. indicated that under highly alkaline conditions in situ generation of a surface film on the anode with catalytic properties towards cyanide electrolysis was observed; Copper oxi-hydroxides compounds constitute the surface film developed on the stainless steel anodes, as no traces of N− and C-containing compounds were observed [8]. An investigation of the electrochemical oxidation of copper cyanide was also carried out by Cheng et al. (2002) [7]. This enhanced electrocatalytic activity is believed to be related to the formation of an active copper species.

In a photocatalytic process the primary step following the radiation absorption by the photocatalyst is the generation of electron-hole pairs which must be trapped to avoid recombination. In the case of photoelectrocatalytic process with the application of a positive potential, separation efficiency of the photogenerated e− and h+ was enhanced by the potential gradient. The holes were driven to the catalyst surface and electrons were driven towards the interior of semiconductor, where they can be swept to the counter electrode. The holes can react with the OH− radicals adsorbed onto the catalyst surface, leading to the generation of active OH•.

\[ \text{TiO}_2 + \text{h}^+ \rightarrow \text{TiO}_2 + e_{\text{CB}} + \text{h}_{\text{VB}}^+ \]  

(1)

\[ \text{TiO}_2 - \text{OH}^- + \text{h}^+ \rightarrow \text{TiO}_2 - \text{OH}^* \]  

(2)

It has been shown in several studies that CNO− was the first product in the photocatalytic oxidation of cyanides in the presence of TiO2 in aqueous medium; the oxidation of C− proceeded via photoholes preferably than via photogenerated hydroxyl radicals [30,31]. Therefore, it was concluded that the holes played the key role in the PEC oxidation of C− into OCN−.

\[ \text{CN}^- + 2\text{OH}^- + 2\text{h}^+ \rightarrow \text{CNO}^- + \text{H}_2\text{O} \]  

(3)

Meantime, a similar phenomenon occurred that the Cu oxi-hydroxides were generated onto the TNTs anode in the PEC oxidation of Cu-cyanide complexes, which can be seen from the black surface coating onto the TNTs electrode clearly. Furthermore confirmation by Cu mass distribution and SEM-EDX analysis of the anode and cathode variation will be given subsequently.

A mechanism accounting for the in-situ formation of copper (hydro) oxides on the anode during the electrochemical oxidation of copper complex cyanide solutions under alkaline conditions has been proposed [32], which can be expressed in terms of the following sequence of reactions:

\[ \text{Cu(CN)}_{(1-n)} + 2\text{H}_2\text{O} \rightarrow \text{CuOOH} + 3\text{H}^+ + n\text{CN}^- + 2\text{e}^- \]  

(4)

Furthermore, the data in Fig. 4(a) were stimulated using the first-order kinetics equation. The results indicated that the removal of total cyanides and Cu recovery constants followed the first-order kinetics reaction. As shown in Fig. 4(b), the kinetics constants of the removal of total cyanides and Cu recovery increase with the applied bias potentials. Similar variation trend was observed and discussed in our previous work [29].
individual oxidation of Cu-cyanide complexes. In another way, the TNTs anode will be covered by the generated Cu-oxides, inhibiting the PEC oxidation of Cu-cyanide complexes. With respect to the Cu recovery, it was desired to be deposited onto the cathode with the zero value. The performance of the process under very alkaline conditions was not advantageous and did not give the possibility of

![Fig. 4. (a) Effect of applied bias potentials on the oxidation efficiency of Cu-cyanide complexes and Cu recovery efficiencies; (b): the first-order kinetic constant of the oxidation of Cu-cyanide complexes and Cu recovery under various applied bias potential ([Cu(CN)₃] = 0.5 mM, [NaCN] = 1.0 mM, [Na₂SO₄] = 1.0 mM, pH = 11.0).](image)

![Fig. 5. Generation of NH₄-N and OCN⁻ in the PEC oxidation of Cu-cyanide complexes under various applied bias potentials ([Cu(CN)₃] = 0.5 mM, [NaCN] = 1.0 mM, [Na₂SO₄] = 1.0 mM, pH = 11.0).](image)

![Fig. 6. PEC treatment of Cu-EDTA and Cu recovery at the TiO₂ nanotube electrode at an applied bias potential of 1.5 V ([Cu-EDTA] = 0.5 mM; NaClO₄ = 1 mM).](image)

the recovery and reuse of copper due to the electrodeposition of metallic copper occurring at the cathode.

3.3. Individual oxidation of Cu-EDTA

Cu-EDTA complexes were frequently used in the electroplating industry. Herein, individual PEC oxidation of Cu-EDTA at the TNTs electrode at various pH conditions was investigated. It can be seen that the PEC oxidation of Cu-EDTA performs better at pH = 3 than at pH = 7 and pH = 11. Similar variation trend of Cu recovery with the pH variation is also observed (Fig. 6). Distribution of Cu in the solution, anode surface, and cathode surface is calculated and the result is presented in Fig. 7. At pH 3, nearly 80% Cu is deposited onto the cathode. By contrast, the deposited amount of Cu at the TNTs anode decreases with increase of solution pH values.

At high pH conditions, the liberated Cu²⁺ was readily adsorbed onto the TNTs anode or hydrolyses occurs easily, leading to the generation of Cu oxides or Cu hydro-oxides, which may deposit onto the anode or precipitate in the solution. Therefore, the oxidation of cyanide ions by photoelectrocatalytic process was inhibited. By contrast, at low pH conditions, liberated Cu²⁺ ions were quickly released into the solution and easily electrodeposited onto the cathode. Thus, cyanide ions can be efficiently oxidized through the photoelectrocatalytic process. Similar effects of pH values on the TiO₂ photocatalytic oxidation of EDTA and several metal complexes of EDTA were observed [33,34].

![Fig. 7. Cu distribution at various pH conditions by PEC treatment at the applied bias potential of 1.5 V for 120 min ([Cu-EDTA] = 0.5 mM; NaClO₄ = 1 mM).](image)
the complexes

The complexes of various Fig.

Simultaneous efficiency of pH ratio of [Na2SO4] Concentration of [EDTA]: [CN]: [Cu (CN)3]− = 0.5 mM; [NaCN] = 1.0 mM; [Na2SO4] = 1.0 mM; pH = 11.0).

3.4. Simultaneous oxidation of Cu-cyanide and Cu-EDTA complexes

Simultaneous PEC oxidation of Cu-cyanides and Cu-EDTA complexes was performed at various ratios of [EDTA]: [CN−] at the constant applied bias and pH conditions. It can be seen from Fig. 8(a) that the removal efficiencies of total cyanide increase with the ratio of [EDTA]: [CN−]. Similar removal trend of Cu recovery efficiency is also observed. At the ratio of [EDTA]: [CN−] = 5:1, the recovery efficiency of Cu is nearly 90%. The first-order kinetic constants with the various ratio of [EDTA]: [CN−] was also given in Fig. 8(b). It is clear that the removal efficiency of total cyanide ions and Cu recovery increases with the increased ratio of [EDTA] to [CN−]. As shown in Fig. 9, with the increase of the ratio of [EDTA]: [CN−], the generated amounts of the OCN− intermediate increase gradually. Similarly, the variation trend of NH4+−N amount generated is also observed, which may be the oxidation results of Cu-EDTA.

The Cu mass distribution at the various ratios of [EDTA] to [CN−] was investigated and the results were presented in Fig. 10. Without EDTA, most of Cu is deposited onto the anode. By contrast, only nearly 10% Cu is deposited onto the anode at the [EDTA]: [CN−] = 1:3. Furthermore, at the [EDTA]: [CN−] ratio of 5:1, removed Cu is nearly completely recovered at the cathode.

The effect of EDTA on the photocatalytic oxidation of cyanide has been examined at different molar ratios of EDTA to cyanide [30]. Their results indicated that the presence of EDTA in the reaction mixture reduced the photocatalytic oxidation rate of cyanide and the decrease was not proportional to the molar ratio of EDTA to cyanide. In our previous work on the oxidation of Cu-cyanide complexes by H2O2 under alkaline conditions in the presence of EDTA/pyrophosphate, the results indicated that Cu-cyanide complexes oxidation was accelerated in the presence of EDTA or pyrophosphate [35]. The strong bonding of Cu(II) to EDTA suppressed decomposition of H2O2 into O2 and enhanced the effective utilization of H2O2 for cyanide destruction.

Herein, with the CN− oxidation into OCN−, the complexation reaction of the liberated Cu(II) with EDTA occurred. Formation of Cu-oxi-hydroxide onto the TNTs anode was inhibited. Thus, the PEC oxidation of CN− and generated Cu-EDTA can proceed continuously. With the oxidation of Cu-EDTA, liberated Cu²⁺ ions were electrochemically deposited onto the cathode rather than the formation of Cu-oxi-hydroxide on the TNTs anode.

3.5. SEM and EDX analysis of the anode and cathode surfaces

Furthermore, the surface variations of the anode and cathode under various reaction conditions were checked. As shown in Fig. 11, a large amount of Cu oxides is deposited onto the TNTs anode in the PEC oxidation of Cu-cyanide complexes for 120 min. Meanwhile, a small amount of Cu oxides is also deposited onto the stainless steel cathode. The results were furthermore confirmed by the EDX analysis.
In the case of individual PEC oxidation of Cu-EDTA, it can be seen that a large amount of Cu is deposited onto the stainless steel cathode and nearly the cathode is completely covered. By contrast, little amount of Cu-oxide is observed on the surface of TNTs anode (Fig. 12). This result was similar with the result presented in Fig. 6 on the Cu mass distribution.

In the case of PEC oxidation of Cu-EDTA and Cu-cyanide complexes at the ratio of [EDTA]: [CN\(^-\)] = 5:1, the surface of the TNTs anode and stainless steel cathode was examined by SEM-EDX analysis. As shown in Fig. 13, parts of the TNTs anode surfaces are covered by the Cu-oxides particles. By contrast, the cathode is also covered by the Cu-oxide particles. In comparison with the individual oxidation of Cu-cyanide, the deposition of Cu-oxides onto the TNTs anode is inhibited and electro-deposition of Cu onto the cathode with the zero value is achieved.

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**Fig. 11.** SEM and EDX analysis of the TNTs anode (up) and cathode (down) in the PEC oxidation of Cu-cyanide complexes at an applied bias potential of 1.5 V ([Cu\((CN)_{12}^+\)] = 0.5 mM, [NaCN] = 1.0 mM, [Na\(_2\)SO\(_4\)] = 1.0 mM, pH = 11.0).

**Fig. 12.** SEM and EDX analysis of the TNTs anode (up) and cathode (down) in the PEC oxidation of Cu-EDTA complexes at 1.5 V applied bias potential ([Cu-EDTA] = 0.5 mM; NaClO\(_4\) = 1 mM, pH = 7.0).
4. Conclusions

In the individual PEC oxidation of Cu-cyanides complexes, Cu oxides formed at the TNTs anode with the cyanide destruction; deposition of Cu onto the cathode was also observed. By contrast, the Cu-EDTA complexes were destroyed by the PEC process using TNTs anode with the simultaneous recovery of Cu onto the cathode. In the case of Cu-cyanides and Cu-EDTA, the presence of EDTA increased the oxidation efficiency of \( \text{CN}^- \) to \( \text{OCN}^- \) ions and Cu recovery onto the cathode. And, EDTA in the reaction mixture reduces the deposition of Cu oxides onto the TNTs anode. It was concluded that the continuous degradation of metal complexes containingcyanides and EDTA to below legal emission levels may be feasible.

Acknowledgments

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References

[1] P.R. Dash, A. Gaur, G. Balomajumder, Cyanide in industrial wastewater and its removal: a review on biotreatment, J. Hazard. Mater. 163 (2009) 1–11.
[2] J.R. Parga, D.L. Cocke, Oxidation of cyanide in a hydrocyclone reactor by chlorine dioxide, Desalination 140 (2001) 289–296.
[3] J. Shen, H. Zhao, H.B. Cao, Y. Zhang, Y.S. Chen, Removal of total cyanide in coking wastewater during coagulation process: significance of organic polymers, J. Environ. Sci-China 26 (2014) 231–239.
[4] G.T. Rogers, K.J. Taylor, The electrodeposition of copper from alkaline cyanide solution-1: the effect of trace selenide, Electrochim. Acta. 20 (1975) 695–702.
[5] L. Szpyrkowicz, F. Zilio-Grandi, S.N. Kaul, S. Rigozu-Stern, Electrochemical treatment of copper cyanide wastewaters using stainless steel electrodes, Water Sci. Technol. 38 (1998) 261–268.
[6] U.B. Ojikutu, E. Torii, S. Koparal, Removal of cyanide by anodic oxidation for wastewater treatment, Water Res. 33 (1999) 1851–1856.
[7] S.C. Cheng, M. Gattrell, T. Guenna, B. MacDougall, The electrochemical oxidation of alkaline copper cyanide solutions, Electrochim. Acta 47 (2002) 3245–3256.
[8] L. Szpyrkowicz, F. Ricci, M. Dí, R.M.S. Montermor, Characterization of the catalytic films formed on stainless steel anodes employed for the electrochemical treatment of cuprocyanide wastewaters, J. Hazard. Mater. 119 (2005) 145–152.
[9] A.J.B. Dutra, G.P. Rocha, F.R. Pombo, Copper recovery and cyanide oxidation by electrowinning from a spent copper-cyanide electroplating electrolyte, J. Hazard. Mater. 152 (2008) 648–655.
[10] D.H. Kim, M.A. Anderson, Photoelectrocatalytic degradation of formic acid using a porous TiO2 thin film electrode, Environ. Sci. Technol. 28 (1994) 479–483.
[11] X. Quan, S.G. Yang, X.L. Ruan, H.M. Zhao, Preparation of titania nanotubes and their environmental applications as electrode, Environ. Sci. Technol. 39 (2005) 3770–3775.
[12] H.W. Sun, G.Y. Li, X. Nie, H.X. Shi, W. Po-K. H.J.Z. hao, n, Systematic approach to in-depth understanding of photoelectrocatalytic bacterial inactivation mechanisms by tracking the decomposed building blocks, Environ. Sci. Technol. 48 (2014) 9412–9419.
[13] R. Daghrir, P. Drough, D. Robert, Photoelectrocatalytic technologies for environmental applications, J. Photoch. PhotoBio. A 238 (2012) 41–52.
[14] P.A. Christensen, T.P. Curtis, T.A. Egerton, S.A.M. Kosa, J.R. Tinlin, Photoelectrocatalytic and photocatalytic disinfection of E. coli suspensions by titanium dioxide, Appl. Catal. B: Environ. 41 (2003) 371–386.
[15] L.E. Fraga, M.A. Anderson, M.L.P.M.A. Beatriz, F.M.M. Paschoal, L.P. Romão, M.V. B. Zanoni, Evaluation of the photoelectrocatalytic method for oxidizing chloride and simultaneous removal of microcystin toxins in surface waters, Electrochim. Acta 54 (2009) 2069–2076.
[16] E. Valova, J. Georgieva, S. Armanov, S. Sotiropoulos, A. Hubin, K. Baert, M. Raes, Morphology, structure and photoelectrocatalytic activity of TiO2/WO3 coating obtained by pulsed electrodeposition onto stainless steel, J. Electrochem. Soc. 157 (2010) D309–D315.
[17] J. Manugùa, P. Christensen, T. Egerton, H. Purnam, Synthesis, characterization and activity of photocatalytic sol–gel TiO2 powders and electrodes, Appl. Catal. B: Environ. 89 (2009) 273–283.
[18] J. Georgieva, E. Valova, S. Armanov, N. Philippidis, I. Poulos, S. Sotiropoulos, Bi-component semiconductor oxide photoanodes for the photoelectrocatalytic oxidation of organic solutes and vapours: A short review with emphasis to TiO2–WO3 photoanodes, J. Hazard Mater. 211 (2012) 30–46.
[19] M.E. Osugi, K. Rajeshwar, E.R.A. Ferraz, D.P. de Oliveira, Â.R. Araújo, M.V.B. Zanoni, Comparison of oxidation efficiency of disperses dyes by chemical and photoelectrocatalytic chlorination and removal of mutagenic activity, Electrochim. Acta. 54 (2009) 2086–2093.
[20] M.F. Brugnera, K. Rajeshwar, J.C. Cardoso, M.V.B. Zanoni, Bispheon A removal from wastewater using self-organized TiO2 nanotubular array electrodes, Chemosphere 78 (2010) 569–575.
[21] S.N. Chai, G.H. Zhao, Y.N. Zhang, Y.J. Wang, F.Q. Nong, M.F. Li, D.M. Li, Selective photoelectrocatalytic degradation of recalcitrant contaminant driven by an n–p heterojunction nan electrode with molecular recognition ability, Environ. Sci. Technol. 46 (2012) 10182–10190.
Comparative examination of TiO2 nanotube, Cu2O/TiO2/carbon and TiO2 nanotube arrays: effects of electrolyte temperature and anodization potential. J. Phys. Chem. C 113 (2009) 4026–4030.

N. Xin, G.Y. Li, M.H. Gao, H.W. Sun, X.L. Liu, H.J. Zhao, P.K. Wong, T.C. An, Comparative study on the photoelectrocatalytic inactivation of Escherichia coli K-12 and its mutant Escherichia coli BW25113 using TiO2 nanotube as a photocathode. Appl. Catal. B: Environ. 147 (2015) 562–570.

T.T. Li, X.Y. Li, Q.D. Zhao, Y. Shi, W. Teng. Fabrication of n-type CuInS2 modified TiO2 nanotube arrays heterostructure photocathode with enhanced photoelectrocatalytic properties. Appl. Catal. B: Environ. 156 (2015) 362–370.

L.S. Clescerl, A.E. Greenberg, A.D. Eaton, Standard methods for the examination of water and wastewater, United Book Press Inc., Baltimore, Maryland, United States, 1998.

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[22] Y.B. Wang, Y.N. Zhang, G.H. Zhao, H.Y. Tian, H.J. Shi, T.C. Zhou, Design of a novel CuO/TiO2/carbon aerogel electrode and its efficient electrosorption-assisted visible light photocatalytic degradation of 2,4,6-trichlorophenol. ACS. Appl. Mater. Inter. 4 (2012) 3965–3972.

[23] J.M. Macak, H. Tsuchiya, L. Taveira, S. Aldabgerrova, P. Schmuki, Smooth anodic TiO2 nanotube, Angew. Chem. Int. Ed. 44 (2005) 7463–7465.

[24] G.K. More, K. Shankar, M. Paulose, O.K. Varghese, C.A. Grimes, Use of highly ordered TiO2 nanotube arrays in dye-sensitized solar cells, Nano. Lett. 6 (2006) 215–218.

[25] J. Wang, Z.Q. Lin, Anodic Formation of Ordered TiO2 Nanotube Arrays: Effects of Electrolyte Temperature and Anodization Potential. J. Phys. Chem. C 113 (2009) 4026–4030.

[26] N. Xin, G.Y. Li, M.H. Gao, H.W. Sun, X.L. Liu, H.J. Zhao, P.K. Wong, T.C. An, Comparative study on the photoelectrocatalytic inactivation of Escherichia coli K-12 and its mutant Escherichia coli BW25113 using TiO2 nanotube as a photocathode. Appl. Catal. B: Environ. 147 (2015) 562–570.

[27] T.T. Li, X.Y. Li, Q.D. Zhao, Y. Shi, W. Teng, Fabrication of n-type CuInS2 modified TiO2 nanotube arrays heterostructure photocathode with enhanced photoelectrocatalytic properties. Appl. Catal. B: Environ. 156 (2015) 362–370.

[28] L.S. Clescerl, A.E. Greenberg, A.D. Eaton, Standard methods for the examination of water and wastewater, United Book Press Inc., Baltimore, Maryland, United States, 1998.

[29] X. Zhao, L.B. Guo, B.F. Zhang, H.J. Liu, J.H. Qu, Photoelectrocatalytic oxidation of Cu(II)-EDTA at the TiO2 electrode and simultaneous recovery of Cu(II) by electrodeposition, Environ. Sci. Technol. 47 (2013) 4480–4486.

[30] K. Osathaphan, B. Chucherdowatansak, P. Rachdawong, V.K. Sharma, Photocatalytic oxidation of cyanide in aqueous titanium dioxide suspensions: Effect of ethylenediaminetetraacetate, Sol. Energy 82 (2008) 1031–1036.

[31] M.A. Barakat, Y.T. Chen, C.P. Huang, Removal of toxic cyanide and Cu(II) ions from water by illuminated TiO2 catalyst, Appl. Catal. B: Environ. 53 (2004) 13–20.

[32] L.G. Casella, M. Gatta, Anodic electrodeposition of copper oxide/hydroxide films by alkaline solutions containing cuprous cyanide ions, J. Electroanal. Chem. 494 (2000) 12.

[33] T.H. Madden, A.K. Datye, M. Fulton, Oxidation of metal-EDTA complexes by TiO2 photocatalysis, Environ. Sci. Technol. 31 (1997) 3475–3481.

[34] A.P. Davis, D.L. Green, Photocatalytic oxidation of Cadmium-EDTA with titanium dioxide, Environ. Sci. Technol. 33 (1999) 609–617.

[35] F.Y. Chen, X. Zhao, H.J. Liu, J.H. Qu, Enhanced destruction of Cu(CN)2– by H2O2 under alkaline conditions in the presence of EDTA/pyrophosphate, Chem. Eng. J. 253 (2014) 478–485.