Photocatalytic conversion of ethylenediaminetetraacetic acid dissolved in real electroplating wastewater to hydrogen in a solar light-responsive system
En-Chin Su, Ju-Ting Lee, Yi-Jean Gong, Bing-Shun Huang and Ming-Yen Wey

ABSTRACT
A sustainable and multifunctional photocatalysis-based technology has been established herein for simultaneous hydrogen generation and oxidation of ethylenediaminetetraacetic acid (EDTA) in real electroplating wastewater. When the photocatalyst concentration was 4 g/L and electroplating wastewater pH was 6, optimal adsorptions of EDTA$^{2-}$, H$^+$, and H$_2$O were observed, while hydrogen generation efficiency reached 305 µmol/(h g). Owing to EDTA oxidation and occupation of the active sites of the photocatalyst by Ni ions or Ni-EDTA chelates, the charge separation and adsorptions of H$^+$ and H$_2$O decreased, reducing hydrogen generation efficiency with time. The lower EDTA and Ni concentrations in treated wastewater showed that photocatalytic conversion of EDTA in real electroplating wastewater to enhance hydrogen generation efficiency can be a practical alternative energy production technology. This study provided a novel idea to enhance the value of electroplating wastewater, to build a hydrogen generation route with no consumption of a valuable resource, and to reduce EDTA and Ni concentrations in electroplating wastewater.

Key words | chemical oxygen demand reduction, ethylenediaminetetraacetic acid, nickel adsorption, photocatalyst, real electroplating wastewater, waste-to-hydrogen

INTRODUCTION
Hydrogen is considered a promising energy resource because of its high heating value, energy conversion, and renewability (Fujishima & Honda 1972; Abanades & Flamant 2006; Yeh et al. 2014). Among the current technologies for hydrogen generation (e.g. petroleum steam reforming, biomass gasification, bio-hydrogen, electrolysis, and photocatalysis) (Bai et al. 2011; Pereira et al. 2011; Parthasarathy & Narayanan 2014; Belhadi et al. 2015), photocatalysis is considered one of the most promising because of renewable starting materials and clean procedure (Babu et al. 2012; Dhanasekaran & Gupta 2012; Acar et al. 2016; Castro et al. 2017). In a photocatalyst, excitation by light induces transition of photogenerated electrons from the valence band (VB) to the conduction band (CB). Then, the photogenerated holes (h$^+$) and electrons (e$^-$) move to the photocatalyst surface and participate in H$_2$O oxidation and hydrogen generation, respectively (Saqib et al. 2016; Su et al. 2016; Ferrari-Lima et al. 2017). Moreover, due to the strong redox potential of the photocatalyst, organic pollutant (e.g. pharmaceutical wastewater and dye wastewater) treatment by photocatalysis has also been widely discussed (Boutra & Trari 2017; Mahlangu et al. 2017; Zhang et al. 2017a, 2017b; Gao et al. 2018; Huo et al. 2018; Ramezanalian-deh & Manteghi 2018; Sun et al. 2018).

The hydrogen generation activity of a photocatalyst is usually limited due to a fast electron-hole recombination rate (Mohamed et al. 2016). Modifying the surface of a photocatalyst with a metal with greater electron affinity than Ti can facilitate the migration of photogenerated electrons (e$^-$) from the CB of the photocatalyst to the surface, thereby inhibiting charge recombination and enhancing hydrogen generation efficiency (Badawy et al. 2014; Chowdhury et al. 2017; Ismail et al. 2017; Nasirian & Mehrvar 2017; Zhang et al. 2018). Previous studies have also indicated that adding methanol, ethanol, or ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, Na$_2$C$_{10}$H$_{14}$O$_8$N$_2$) as an
recycling electroplating wastewater and reusing the EDTA in the electroplating wastewater as an electron donor (hole scavenger) would confer three advantages to the photocatalytic hydrogen generation process: (1) the requirement for improvement of charge separation would be satisfied without consumption of a valuable resource; (2) EDTA could be oxidized during photocatalysis, resulting in decreased COD in the electroplating wastewater; and (3) the metal may adsorb on the photocatalyst surface, lowering the complexity and cost of the wastewater treatment process before discharge.

To the best of our knowledge, the photocatalytic conversion of EDTA in real electroplating wastewater for enhancement of hydrogen generation efficiency has rarely been studied. In this study, the Ni ions and EDTA molecules, contained in the recycled electroplating wastewater, were chosen as the electron donors, and a solar-light-responsive platinum/nitrogen-doped TiO2/strontium composite (Pt/N-TiO2/SrTiO3) (Huang et al. 2015), which was developed in our previous study, was chosen as the photocatalyst. Simulated solar light was applied as the light source to provide a new perspective on the development of a green and practical waste-to-hydrogen conversion technology. The mechanism for the photocatalytic conversion of EDTA dissolved in real electroplating wastewater to hydrogen in a solar-light-responsive system is schematically shown in Figure 1. The influences of photocatalyst concentration and electroplating wastewater pH on the hydrogen generation efficiency have been discussed. The changes in EDTA conversion and nickel adsorption with time were also evaluated.

Figure 1 | Illustration of the mechanism for the photocatalytic conversion of EDTA dissolved in real electroplating wastewater to hydrogen in a solar light-responsive system.
MATERIALS AND METHODS

Electroplating wastewater sampling

Electroplating wastewater samples were obtained from a camera lens factory located in the Changhua Coastal Industrial Park in Taiwan. The electroplating process involved degreasing, acid washing, electroplating, and electroless plating steps. In the electroplating step, NiSO₄ and NiCl₂ were used as precursors for formation of the Ni layer on the material, and EDTA-2Na was used as a buffer for Ni ion concentration control. Before the electroless plating step, the material coated with the Ni layer was washed by immersing sequentially in several clean water tanks. The electroplating wastewater used in this study was a mix of wastewater collected from these tanks.

Photocatalytic hydrogen generation test

The appropriate amount of solar-light-responsive Pt/N-TiO₂/SrTiO₃ photocatalyst, developed in our previous study, was added to a reactor containing 50 mL of the electroplating wastewater. The simulated solar light lamp (420 W/m², XHA500) was fixed 10 cm above the transparent reactor. The reaction temperature was maintained at 20°C using a circulating bath. The suspension was deaerated with a N₂ flow in the dark before photocatalytic H₂ production. The gases produced were sent automatically to an online gas chromatograph (gas chromatograph with a thermal conductivity detector, PerkinElmer Clarus 500, Carboxen 1000 column, N₂ carrier) every 10 min to determine the hydrogen concentration.

Electroplating wastewater composition analysis

The pH of the electroplating wastewater was measured using a pH meter (CLEAN Instruments, PH500). A standard method of the American Society for Testing and Materials (D3113-92) was used to determine the total concentration of the EDTA sodium salt in the electroplating wastewater. The Ni ion concentration in the electroplating wastewater was determined using a water quality analyzer (PhotoLab S6, Suntex). First, the pH of the electroplating wastewater containing Ni ions was confirmed to be in the range of 3–8. If required, dilute sodium hydroxide solution or sulfuric acid solution was added dropwise to adjust the pH. Then, Ni ion concentration of the electroplating wastewater was confirmed to be in the range of 0.1–6.0 mg/L. If required, the wastewater sample was diluted with deionized water. The sample (5 mL) was added to a reaction cell containing a solution of iodine and dimethylglyoxime, in which the Ni ions are oxidized by iodine and then reacted with dimethylglyoxime to produce a red-brown complex that is determined photometrically.

RESULTS AND DISCUSSION

Influence of photocatalyst concentration on hydrogen generation

Different amounts of the photocatalyst were added to 50 mL of real electroplating wastewater to investigate the influence of photocatalyst concentration on hydrogen generation efficiency; the average hydrogen generation rates obtained after a reaction time of 90–120 min were chosen as the representative values to evaluate the performance. The hydrogen generation efficiencies (Figure 2) indicate that the photocatalyst exhibited good activity for production of hydrogen from EDTA in real electroplating wastewater. The results indicated that the EDTA molecules in real electroplating wastewater play a pivotal role, assisting in the photocatalytic production of hydrogen. The rate of hydrogen generation increased upon increasing the photocatalyst concentration from 1.0 to 4.0 g/L due to increased number of available active sites and photogenerated electrons at higher photocatalyst concentrations. The highest average hydrogen generation rate (112 µmol/(h g)) was obtained for a photocatalyst concentration of 4.0 g/L.

Figure 2 | Influence of photocatalyst concentration on hydrogen generation.
concentration, resulting in enhanced reaction probability between photogenerated electrons and holes and H$_2$O molecules or H$^+$ ions and increased hydrogen generation efficiency. Moreover, more photogenerated electron–hole pairs were produced at higher photocatalyst concentrations, which facilitated the photocatalytic oxidation of H$_2$O molecules and photocatalytic reduction of H$^+$ ions, leading to enhanced hydrogen generation efficiency. However, when the concentration of photocatalyst was increased further to 8.0 g/L, the hydrogen generation rate decreased to 86 µmol/(h g). Under the same irradiation conditions, the photon count was fixed and some of the photocatalyst could not be excited by the fixed photon count when an excess amount was used. Moreover, the excess photocatalyst increased the turbidity of the solution, resulting in a screening effect. This hindered light penetration (Reddy et al. 2016; Sudrajat et al. 2016), which reduced the excitation probability of the photocatalyst, leading to decreased hydrogen generation efficiency. Furthermore, when the photocatalyst concentration is too high, the activated TiO$_2$ molecules will be deactivated by the reaction between activated TiO$_2$ molecules and ground-state TiO$_2$ molecules during the stirring process, resulting in inhibited photocatalytic hydrogen generation activity (Neppolian et al. 2002).

Influence of pH value on hydrogen generation

To elucidate the influence of the wastewater pH on the activity of the photocatalyst for hydrogen generation, we adjusted the pH from 9.75 to 5, 6, and 7 using a dilute HCl solution. The average hydrogen generation rates after a reaction time of 90–120 min were chosen as the representative values to evaluate the performance. The hydrogen generation efficiencies (Figure 3) indicate that the photocatalyst exhibited better activities when the pH of the wastewater was 5, 6, and 7, and the corresponding average hydrogen generation rates were 275, 305, and 273 µmol/(h g), which were 2.4–2.7 times higher than that observed when the wastewater pH was 9.75. This trend was attributable to the variation in the surface charge of the photocatalyst. Excess adsorption of anions (electron donors) on the photocatalyst surface is more likely when the reaction pH is lower than the photocatalyst zeta potential (pH$_{ZPC}$) (Kumari et al. 2015; Acisli et al. 2016). The anions adsorbed on the photocatalyst surface occupy the active sites, leading to hindered adsorption of H$^+$ ions and H$_2$O molecules. Moreover, the surface charge of the photocatalyst becomes negative when the reaction pH is higher than the photocatalyst pH$_{ZPC}$, leading to reduced adsorption of anions (electron donors). The pH$_{ZPC}$ of the photocatalyst was 6. When the reaction pH was close to 6, both the interference by excess EDTA$^{2-}$ anions and the hindered adsorption of EDTA$^{2-}$ anions on the photocatalyst surface could be avoided, resulting in appropriate EDTA$^{2-}$ adsorption, good charge separation, and good hydrogen generation efficiency.

EDTA conversion with time

The results shown in Figure 4 indicate that both hydrogen generation rate and residual EDTA concentration decreased gradually with increasing reaction time. To confirm whether the pH changed during the photocatalytic process and to check whether this change was the critical factor interfering with the photocatalytic performance, we prepared simulated electroplating wastewater with the same initial EDTA concentration, initial Ni concentration, and initial pH as in
the real electroplating wastewater used for the tests. However, the results showed that the change in pH of the wastewater samples was negligible after reaction for 1–4 h, indicating that the change in pH during the photocatalytic process was not the critical factor interfering with photocatalytic performance.

As mentioned in our previous reports (Su et al. 2015, 2016), since the EDTA molecules decompose into NH₃, CO₂, and H₂ by ·OH and superoxide radicals ·O₂ during the reaction, the EDTA concentration would decrease with increasing reaction time. Furthermore, owing to the adsorption of the metal ions or oil molecules in real wastewater on the photocatalyst surface, the number of active sites on the photocatalyst surface would decrease gradually, resulting in hindered adsorption of H⁺ ions and H₂O molecules and reduction in hydrogen generation activity. This result indicated that EDTA molecules could be photo-oxidized by the photocatalyst during photocatalytic hydrogen generation, which was a good method to lower the COD of the electroplating wastewater. The EDTA concentration difference after 1 h, for example, was 43 mg/L, implying that 6.39 × 10⁻⁶ moles of Na₂EDTA were consumed in a 50 mL reaction solution during the photocatalytic reaction. Theoretically, the oxidation of one mole of EDTA-2Na (Na₂\(\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2\cdot2\text{H}_2\text{O}\)) can provide seven moles of hydrogen. However, the amount of hydrogen produced by the oxidation of EDTA in real wastewater (44.75 µmol H₂) was far lower than that expected based on the hydrogen generation rate of 343 µmol/(h g) after reaction for 1 h. This result shows that the EDTA in the real wastewater acted as a hole scavenger, and most of the hydrogen was produced by photocatalytic water splitting.

**Nickel adsorption with time**

Figure 5 shows that the nickel concentration decreased after the photocatalytic reaction. The photocatalyst shows both redox ability and adsorption ability (Huang et al. 2012; Lee et al. 2015) during the photocatalytic reaction. The decreased nickel concentration indicated that the as-prepared photocatalyst could also act as an adsorbent for the free Ni ions or the Ni-EDTA chelate during the photocatalytic reaction. The slight increase in the concentration of residual Ni ions after a reaction time of 2 h might be attributed to occasional desorption of Ni ions from the photocatalyst surface during stirring. It was also observed that the hydrogen generation rate decreased with decreasing residual nickel concentration, indicating that the adsorptions of H⁺ ions and H₂O molecules were inhibited owing to the occupation of active sites by the Ni ions, Ni-EDTA chelates, or oil molecules, leading to lower hydrogen generation efficiency. The decreased EDTA and Ni concentrations in the treated electroplating wastewater indicated that the photocatalytic hydrogen generation system designed in this study provided a method to lower both the complexity and cost of electroplating wastewater treatment before discharge.

**CONCLUSIONS**

A sustainable and practical technology for simultaneous hydrogen generation and oxidation of EDTA dissolved in real electroplating wastewater was established herein. The EDTA molecules in the electroplating wastewater could effectively lower the charge recombination rate, resulting in good hydrogen generation efficiency. During the photocatalytic hydrogen generation process, the EDTA could be oxidized into NH₃, CO₂, and H₂, and Ni ions or Ni-EDTA chelates could be removed from the electroplating wastewater by adsorption on the photocatalyst surface, thus lowering the complexity and cost of electroplating wastewater treatment before discharge.

When the photocatalyst concentration was 4 g/L and the pH of the electroplating wastewater was close to the pH_{ZPC} of the photocatalyst, the optimal adsorptions of EDTA\(^{2-}\) anions, H⁺ ions, and H₂O molecules on the photocatalyst were observed, resulting in inhibited charge recombination and good hydrogen generation efficiency. Moreover, the results indicated that owing to the oxidation of EDTA molecules and the occupation of the active sites by the Ni ions or Ni-EDTA chelates, charge separation and adsorptions of H⁺ ions and H₂O molecules decreased,
resulting in reduced hydrogen generation efficiency with time.

The decreased EDTA and Ni concentrations in the treated electroplating wastewater indicated that the photocatalytic conversion of EDTA in real electroplating wastewater for enhancement of hydrogen generation efficiency can be a practical alternative energy production technology.

ACKNOWLEDGEMENTS

The authors would like to thank the Ministry of Science and Technology, Taiwan, R.O.C., for providing financial support through grant no. NSC 101-2221-E-005-043-MY3.

REFERENCES


Su, E.-C., Huang, B.-S. & Wey, M.-Y. 2016 Sustainable hydrogen production from electroplating wastewater over a solar light responsive photocatalyst. RSC Adv. 6 (75), 71273–71281.


Zhang, Z., Shao, S., Deng, J., Lu, C., Qin, F. & Quan, W. 2017b Synthesized of ZnWO₄/Ag₃PO₄ p-n heterojunction photocatalyst and enhanced visible-light photocatalytic applications. Water Sci. Technol. 76 (12), wst2017631.
