Simultaneous Electrochemical Oxidation of Methylene Blue and Reduction of CO$_2$
using CNTs/CF electrodes

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Simultaneous degradation of methylene blue (MB) and reduction of CO$_2$ by electrochemical process using CNTs/CF electrodes have been performed in various supporting electrolytes and applied current conditions in this study. The CNTs/CF electrodes have been successfully synthesized by chemical vapor deposition (CVD) method and employed as both cathode and anode in a two-compartment electrochemical cell. The synthesized electrodes were characterized by SEM and FTIR. The electrochemical oxidation efficiency of CNTs/CF electrodes in the anodic cell was evaluated using MB as model compound under electrolytes of H$_2$SO$_4$ and KHCO$_3$ and applied currents of 10, 50 and 100 mA. The electrochemical reduction activity of CNTs/CF electrodes in the cathodic cell was assessed by the conversion of CO$_2$ into CO and oxalic acid, and the generation of H$_2$ under electrolytes of Na$_2$SO$_4$ and KHCO$_3$ and a fixed applied current of 50 mA. The degradation kinetics of MB followed the pseudo-first-order model and the degradation efficiency was significantly affected by applied current rather than the sort of electrolyte under optimum condition. The optimal applied current can promote the high enough production of oxidant but also avoid electrode damage. The synthesized electrode of CNTs/CF combined with the electrochemical systems developed in this study provide a good solution for the simultaneous electrochemical oxidation of organic pollutants and reduction of CO$_2$ to CO to yield H$_2$ and CO, in which reaches the dual benefits of reduction of environmental hazards and production of green energy.

Keywords: Electrochemical oxidation, CO$_2$ reduction, CNTs/CF, Methylene blue.
1. **Introduction**

Wastewater arisen from the textile and dye industries typically possessed color, which the conventional wastewater treatment processes usually ineffectively deal with due to the complex structures [1]. Dye molecules are normally composed of aromatic rings compounds and even metals, which resulted in less biodegradation. The ordinary treatments such as adsorption and coagulation are not commonly sustainable because they are chemical intensive and produce hazardous sludge, respectively [2,3]. Although chemical oxidation with ozone, Fenton's reagent [4] and other advanced oxidation processes have highly efficient, they still contain some disadvantages relating to the high cost and operational problems [5].

In recent decades, new advanced oxidation processes relied on the electrochemical technology have been proposed as effective solutions to deal with refractory organic compounds [6,7]. These methods are based on the electrochemical generation of hydroxyl radical (•OH), a very powerful oxidizing agent which able to destroy organics up to their mineralization [8-10]. Moreover, electrochemical oxidation is also considered as an economical, safe and environmentally friendly technology for the wastewater treatment due to it generates highly reactive species from only electrical current without using other hazardous chemicals to produce the strong oxidants. Electrochemical processes applied in water treatments to oxidize organic pollutants have been demonstrated in many researches indicating that this approach may be feasible for large groups of dye widely used in textile industry [3,11-13].

On the other hand, electrochemical reduction of CO₂ into valuable chemicals has attracted the attention as an innovative approach which utilizes renewable energy to help address the problem of greenhouse gas emissions [14,15]. There are a variety of target products may be produced by
CO\textsubscript{2} reduction, depending on the electron transfer mechanism and operation conditions. In general, the main products generated during CO\textsubscript{2} reduction process are C1 compounds (e.g., carbon monoxide [16], formic acid [17], methanol [18], methane) or C2 compounds (e.g. ethanol, acetate or ethylene). Besides, Hydrogen Evolution Reaction (HER), the side reaction of the electro-reduction process in aqueous solution also leads to the generation of H\textsubscript{2}, which combining with CO can become the feedstock for the synthesis of methanol in Fischer-Tropsch process [19] or syngas [20,21]. It is worth noting that most of these products are high energy-containing products.

Generally, in electrochemical process, the electrode materials play significant roles in both oxidation and reduction processes. Good electrodes for oxidation process should exhibit high electrocatalytic activity toward organics degradation and low activity toward side reactions as Oxygen Evolution Reaction (OER) coupled with high current efficiency in the oxidation process and possess high selectivity toward the desired products in the reduction of CO\textsubscript{2} [22]. Although considerable numbers of studies on the development of novel materials serving as electrodes in electrochemical process have been conducted recently, most of them still suffer from obvious drawbacks including high cost, complicated synthesis procedures, short service life and even some of them may release toxics to the environment [23]. Recently, many studies focus on carbon materials and their applications due to their special characteristics, such as physicochemical stabilities and wide potential window for a variety of redox reactions as compared with other materials [24]. Carbon materials are not only much cheaper due to their abundant sources in nature, but also posse high porosity and large surface area. However, pristine carbon is not suitable to be employed as electrode materials due to the electrochemical inert property [25]. It is reported that converting raw carbon materials to the nanostructure materials make the electronic properties of carbon be changed significantly [26,27]. Particularly, carbon nanotubes (CNTs) are the
promising material to offer high electrical conductivity, large surface area and electrochemical stability, high potential window and the capacity to reversibly adsorb H₂ for CO₂ reduction and organics oxidation. [6,28]. In addition, they have been found to promote electron transfer reactions when used as electrode modifying materials [17]. On the other hand, carbon fiber/cloth (CF) with high strength stiffness and low weight have been widely utilized as fillers to reinforce polymer composites [29] or as the substrate for CNTs growth.

Although a great number of papers related to CO₂ reduction have been published, there are very limited reports on the use of CNTs/CF as the electrode for electrochemical reduction of CO₂ [30]. Therefore, based on the promising properties as above, we carried out investigation on simultaneous electrochemical oxidation of methyl blue (MB) as a model indicator and CO₂ reduction using synthesized CNTs/CF electrode. In the meanwhile, the effects of the key operative parameters such as supporting electrolytes (H₂SO₄, KHCO₃ and Na₂SO₄) and applied current conditions (10 mA, 50 mA and 100 mA) were also investigated in this study.

2. Materials and methods

2.1. CNTs/CF synthesis and Characterization

The CNTs-grown CF (CNTs/CF) was used as both cathode and anode in this study, in which the CNTs have been grown on CF (190 mm × 190 mm, ElectroChem, Inc., USA) via the chemical vapor deposition (CVD) method. The CF was subsequently coated with titanium (Ti) of 75 nm and nickel (Ni) of 15 nm via E-Gun Evaporation System (ULVAC Technologies, Inc., USA). Then, CF coated with Ti and Ni was cut into 30 mm × 10 mm size as one piece and then placed in the quartz chamber of CVD reactor (Jyi-Goang, Enterprise Co. Ltd., Taiwan) for further growth of CNTs. The experimental condition for CNTs growth was as follows: first, the chamber was
flushed with argon of 259 mL min\(^{-1}\) at a heating rate of 72.5 K min\(^{-1}\) until the temperature of 1023 K reached; next, argon of 126 mL min\(^{-1}\) and ammonia of 70 mL min\(^{-1}\) were simultaneously injected into the chamber for 10 min at 1023 K; then, argon of 193 mL min\(^{-1}\), ammonia of 32 mL min\(^{-1}\) and acetylene of 11 mL min\(^{-1}\) were used for the growth of CNTs under a period of 25 mins at a fixed temperature of 1023 K; finally, the reaction stopped and the temperature of the chamber naturally dropped to room temperature and the materials were taken out for use. All the flow rates were controlled by the mass controller (Model: 5850E, Brooks). The morphology and surface functional groups of the obtained materials was characterized by scanning electron microscopy (FE-SEM, JSM-7800F, JEOL) and Fourier-transform infrared spectroscopy (FTIR, FT/IR-460 Plus. Jasco), respectively.

2.2. Electrochemical system

The galvanostatic experiments were conducted at room temperature in a two-compartment cell separated by proton exchange membrane (Nafion 212 membrane, Dupont). The system was batch mode at a solution volume of 100 mL per cell under the magnetic stirring of 300 rpm. The cathodic cell was saturated with high purity CO\(_2\) gas before electrochemical experiments while anodic cell was filled with MB solution at a constant initial concentration of 10 mg L\(^{-1}\). A three-electrode system was used to conduct the degradation experiments, in which CNTs/CF and Ag/AgCl (saturated with 3 M KCl solution) electrodes were used as anode and cathode with geometric area of 3.0 cm\(^2\), and as the reference electrode, respectively. The electrode current was controlled by an electrochemical analyzer (Model: 627D, CH Instruments, Inc., USA). The CVD and electrochemical systems investigated in this study were shown in Figures 1 and 2.
Figure 1. Schematic of CVD experimental apparatus and system in this study.

Figure 2. Schematic of the electrochemical cell and experimental setup used in the experiments.

2.3. Electrochemical oxidation and reduction

All chemicals used in this study was regent grade without further purification. Three kinds of electrolytes, such as KHCO$_3$ (99%, Alfa Aesar) of 0.1 M, H$_2$SO$_4$ (95-97%, Honeywell) of 0.1 M, and Na$_2$SO$_4$ (99%, Merck) of 0.1 M, were investigated to explore the effects of electrolytes on the degradation of MB (reagent grade, Merck) and reduction of CO$_2$ (purity of 99.9%, Nini Air Co. Ltd., Taiwan). The saturation of CO$_2$ was conducted by purging high purity CO$_2$ gas at the rate of 50 mL min$^{-1}$ for 30 min. Electrochemical reactions were carried out under various electrolytes and applied current conditions (10 mA, 50 mA and 100 mA) and samples were withdrawn at the expected time intervals. The concentrations of CO and H$_2$ in gaseous samples and oxalic acid in liquid samples were determined by gas chromatography with thermal conductivity detector (GC/TCD) analyzer (G3440B, Agilent Technologies, Palo Alto, CA, USA) and high performance liquid chromatography (HPLC) with UV/Vis detector (SPD-20 of detector, LC-20ATof HPLC, Shimadzu, Japan), respectively. The columns used for GC/TCD and HPLC/UV analysers were Shincarbon ST 1/16 mesh column and Acclaim™ Organic Acid column, respectively. The carrier gases for H$_2$ and CO were nitrogen, and helium (purity of 99.9%), respectively. Prior to the main column, the gas was purified by renewable gas purification system (G3440-60003, Agilent Technologies). The liquid samples were filtered through a 0.45 µm filter before analysis. The MB concentration at various time intervals was measured by a Vis-UV spectrophotometer (S-3150,
Scinco) with photodiode array detector. All experimental conditions were repeated twice, and the average values were reported with relative error.

3. Results and discussion

3.1. Characterization

The morphology of synthesized CNTs/CF is illustrated in Figure 3. The macroscopic image of CF is shown in Figure 3a, revealing the diameter of the fiber was round 10 µm. After the growth of CNTs on CF, the SEM image indicated that CNTs have been randomly grown and oriented on CF, as indicated in Figure 3b. The diameter of the CNTs was approximate 100 nm and the size was rather uniform (as represented in Figure 3c). The surface of carbon fiber was covered by many layers of carbon nanotubes, leading to considerably increase the surface area. For electrochemical applications, the nanoscale structures of CNTs on CNT/CFs not only provide more active site for the reactions but also enhance the electronic conductivity, which provokes fast transport of electron through the electrolyte/electrode interface during the electrolysis [3].

Figure 3. Morphology of synthesized CNTs/CF electrode (a) SEM image of carbon fiber (CF) (Scale bar, 10 µm, × 800), (b) SEM image (scale bar, 10 µm, × 2,500), and (c) SEM image (scale bar, 100 nm, × 50,000).

The FTIR spectra of materials were used to investigate the surface functionalization, as recorded between 4000-400 cm\(^{-1}\) and illustrate in Figure 4. The main peaks in CF materials observed were 892 cm\(^{-1}\) of =CH & =CH\(_2\) bending vibration, 1090 cm\(^{-1}\) of C-O, 1306 cm\(^{-1}\) & 1452 cm\(^{-1}\) of CH\(_2\) &
CH₃ deformation, 1735 cm⁻¹ of C=O (in COOH), 2349 cm⁻¹ of CO, and 3070 cm⁻¹ of -OH group [31]. The peaks related to -OH groups were quite broad and the appearance of G-band (1452 cm⁻¹) and D-band (1306 cm⁻¹) were fairly coherent. The FTIR results of CNTs/CF and CF electrodes were similar, but there were higher peaks near 2925 cm⁻¹ but lower peaks at 892 cm⁻¹ for the former, representing that the CₓHₓ functional groups on the material surface move towards strong stretching vibration. The C=O peak at 2349 cm⁻¹ of used CNTs/CF (as anode) was higher as compared to those of pristine CF and CNTs/CF, indicating that the CNTs may be damaged and oxidized during the process of electrochemical oxidation of MB so as to make surface characteristics of used CNTs/CF similar to those of pristine CF.

Figure 4. FTIR spectra of CF, fresh CNTs/CF and used CNTs/CF.

3.2. Electrochemical Degradation of Methylene Blue

The oxidation of MB on the anodic surface of CNTs/CF by the adsorbed hydroxyl radicals electro-generated is expressed in Eqs (1-2). Thus, the degradation/oxidation efficiency (DE, %) of MB could be affected by the applied current and the mass transport rate in the solution, of which the definition is as Eq. (3). In addition, the pseudo-first-order kinetic model was employed to describe the degradation rate of MB under various conditions in this study, as Eqs (4-5).

\[
\text{CNTs/CF} + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{CNTs/CF (OH)_{ads}} + \text{H}^+ + \text{e}^- \quad (1)
\]

\[
\text{CNTs/CF (OH)_{ads}} + \text{MB} \rightarrow \text{CNTs/CF} + \text{MBP} \quad (2)
\]
Degradation efficiency, \( \text{DE, \%} = \frac{[MB]_0 - [MB]}{[MB]_0} \times 100\% \) \hspace{1cm} (3)

\[
\frac{-d[C]}{dt} = k_{\text{obs}} \times [C] \hspace{1cm} (4)
\]

\[
\ln \left( \frac{[MB]_0}{[MB]} \right) = k_{\text{obs}} \times t, \text{ with } t = 0, [C] = [MB]_0; t = t, [C] = [MB] \hspace{1cm} (5)
\]

Where, CNTs/CF and MBP present the active sites of the anode and oxidation byproducts; \( [C] \) is the concentration of target compound; \( t \) is the reaction time, \( h \); \( k_{\text{obs}} \) is the rate constant, \( h^{-1} \).

**Figure 5.** The effect of the applied current on the degradation of MB solution under electrolyte KHCO\(_3\) of 0.1 M in the anodic cell. \( \triangle, \Box \) and \( \bigcirc \): applied currents of 10, 50 and 100 mA, respectively.

**Figure 6.** The effect of the applied current on the degradation of MB solution under electrolyte H\(_2\)SO\(_4\) of 0.1 M in the anodic cell. \( \triangle, \Box \) and \( \bigcirc \): applied currents of 10, 50 and 100 mA, respectively.

Impacts of applied currents on the electrochemical degradation of MB were investigated as shown in Table 1 and Figures 5-6. The DE of MB was about 50% - 73% in the investigated conditions and the sort of electrolyte in anodic cell did not significantly affect the maximum efficiency, of which 72% and 73% were for the electrolyte of 0.1 M H\(_2\)SO\(_4\) and 0.1 M KHCO\(_3\), respectively, under the applied current of 50 mA and the electrolyte of 0.1 M H\(_2\)SO\(_4\) in the cathodic cell. Comparing the results of the electrolyte of KHCO\(_3\) and H\(_2\)SO\(_4\), the applied current has a great impact on the DE in both cases. The DE increased from the current of 10 mA to 50 mA due to the
better capability of electron transfer and electro-generation of high oxidizing agents. Obviously, increase of applied current means greater charge and more electro-generation of \(^{\cdot}\)OH in the cell. Thus, the generation of \(^{\cdot}\)OH is directly proportional to the applied current. The result is in agreement with the literature [32], the electrochemical degradation efficiency increased with the increasing applied current by using graphite electrode for phenol removal. However, when the applied current increases from 50 mA to 100 mA, the efficiency of 100 mA was between those of 10 mA and 50 mA in the electrolyte of KHCO\(_3\), and less than that of 10 mA in the electrolyte of H\(_2\)SO\(_4\). This behavior is possibly due to the reason that when applied current abruptly raises, the OER may take place and commonly leads to decreasing current efficiency for the desired reactions [33,34]. In addition, the adsorptive ability and electrocatalytic activity of electrodes can also be influenced by the formation of by-products from polymerization reactions at high applied current so as to restrict the mass transport [35]. Besides, the damages to the anodic electrodes were possibly caused at high applied current, which results in the damage of the electrode surface [36]. As a result, OER, byproducts arisen from polymerization and deterioration of electrode quality make the higher applied current unfavorable for the electrochemical degradation of MB in the solution. The same phenomenon was discovered by the report [37], in which when the electrolysis was conducted at high current densities using glassy carbon electrode, the surface of electrode was blocked by the coverage of insoluble polymeric products which were relatively slow to oxidize or desorb.

The experimental data within reaction time of two hours were collected to calculate the rate constants, as illustrated in Table 1. As mentioned above, as the applied current reaches a certain level, the DE decreases instead. Comparison of the DE of MB in electrolytes of H\(_2\)SO\(_4\) and KHCO\(_3\) under the same applied current, it can be observed that using H\(_2\)SO\(_4\) as supporting
electrolyte could achieve higher DE, indicating that the oxidation of MB seems to be favorable at acidic medium. Besides, the undesired OER reaction which commonly consumes •OH radicals could be inhibited at the acidic condition [38]. Among the conditions investigated in this study, the greatest $k_{obs}$ of 0.63 h$^{-1}$ was observed in the condition of 0.1 M KHCO$_3$ at the applied current of 50 mA. When using 0.1 M KHCO$_3$ as electrolyte, the degradation kinetics within reaction time of 2 h were faster than those in acidic solution and then the reaction was suppressed and reached the degradation plateau. Moreover, depending on the nature of the supporting electrolyte, except hydroxyl radicals, several oxidants also can be generated from non–oxidants species which then transport toward the bulk of solution [8]. In order to investigate the activity loss of electrodes, the variation of potentials under constant applied current were represented, as shown in Figure 7. After reaction time of 1 hr, the potential dramatically increased and then reached a constant value of 10 V for the case of 100 mV. With respect to the applied current of 50 mV, the same situation occurred at a reaction time of around 2 h and the constant value of 7.5 V. Obviously, the results reveal that the higher current applied, the shorter time the deactivation of electrode reached. In addition, the working time of the electrodes were longer when H$_2$SO$_4$ was used as supporting electrolyte compared to KHCO$_3$.

**Figure 7.** Variation of potential with time during electrochemical oxidation of MB by CNTs/CF electrode under various conditions. Line 1, 2, 3 and 4: electrolyte of 0.1 M KHCO$_3$ and applied current of 100 mA, electrolyte of 0.1 M H$_2$SO$_4$ and applied current of 100 mA, electrolyte of 0.1 M of KHCO$_3$ and applied current of 50 mA, and electrolyte of 0.1 M of H$_2$SO$_4$ and applied current of 50 mA, respectively.
3.3. CO₂ reduction and production of by-products

The production of by-products during CO₂ reduction in the cathodic cell occurred at the same time as electrochemical degradation of MB carried out in the anodic cell. The CO and H₂ arisen from the reduction of CO₂ and electrolysis of H₂O were determined for electrolytes of 0.1 M of KHCO₃ and 0.1 M of Na₂SO₄ in cathodic cell under the applied current of 50 mA and the electrolyte of 0.1 M H₂SO₄ in the anodic cell, as shown in Figures 8 and 9.

**Figure 8.** The CO formation under electrolytes of 0.1 M Na₂SO₄ (□) and 0.1 MKHCO₃ (■) at a fixed applied current of 50 mA during the CO₂ reduction in the cathodic cell.

**Figure 9.** The generation of H₂ under electrolytes of 0.1 M Na₂SO₄ (□) and 0.1 MKHCO₃ (■) at a fixed applied current of 50 mA during the CO₂ reduction in the cathodic cell.

The formation tendency of CO for supporting electrolytes of 0.1 M of KHCO₃ and 0.1 M of Na₂SO₄ seemed to be similar with obvious difference only at a reaction time of 2 hrs. Larger reduction of CO₂ exhibits in the KHCO₃ electrolyte as compared to Na₂SO₄ electrolyte. The CO production increased gradually at the first period of 1.5 h and reached 10.23 mM cm⁻² and 10.63 mM cm⁻² in the Na₂SO₄ and KHCO₃ supporting electrolyte, respectively. However, it should be noticed that the considerable increase of CO production was observed after reaction time of 1.5 h, indicating that CO formation is favorable at high potential. The yield of CO at a reaction time of 3 h were around 30.36 mM cm⁻² and 31.91 mM cm⁻² in Na₂SO₄ and KHCO₃ supporting electrolyte,
respectively, which were much greater than those of pure Cu cathodic electrode (15 µM cm\(^{-2}\)) and Cu coated Cu nano-particles (21 µM cm\(^{-2}\)) under -0.99 V of applied potential [39]. This phenomenon may be due to that the large active area of CNTs significantly enhances the production yield. Furthermore, electrolytes were demonstrated to have significant effects on the nature and amounts of products generated in different electrodes [40,41]. In addition, the size of cation of the electrolytes also played a considerable role. Particularly, the larger cations (Na\(^+\) < K\(^+\) < Rb\(^+\) < Cs\(^+\)) were demonstrated to enhance CO formation [42], which was well in agreement with the results in this study. Figure 9 reveals that the HER was much dependent on the sort of electrolyte. It can be observed that the hydrogen generation increased with reaction time for both supporting electrolytes. Furthermore, KHCO\(_3\) electrolyte showed its greater performance on hydrogen generation as compared with Na\(_2\)SO\(_4\) electrolyte under the same condition. The highest hydrogen generation yield for KHCO\(_3\) and Na\(_2\)SO\(_4\) supporting electrolyte were 18.08 mM cm\(^{-2}\) and 14.78 mM cm\(^{-2}\), respectively, which were 22.6 and 18 times larger than that obtained by a Pt/TiO\(_2\)/CdS/CdSe/PEDOT electrode for photocatalytic hydrogen production [43].

**Figure 10.** The formation of oxalic acid under electrolytes of 0.1 M Na\(_2\)SO\(_4\) (○) and 0.1 MKHCO\(_3\) (△) at a fixed applied current of 50 mA during the CO\(_2\) reduction in the cathodic cell.

The chemicals investigated in this study included formic acid, oxalic acid, methanol, and ethanol, in which only the oxalic acid was determined, as illustrated in Figure 10. The oxalic acid was generated and increased with reaction time in both Na\(_2\)SO\(_4\) and KHCO\(_3\) supporting electrolytes. As the KHCO\(_3\) was adopted as supporting electrolytes, the production of oxalic acid dramatically
raised after reaction time of 2.5 h and reached 2.1 mg L$^{-1}$ cm$^{-2}$ at 3 h which was approximately as 10 times greater as that generated by photocatalytic reduction of CO$_2$ in water using TiO$_2$Npts catalyst [44]. Contrary to the obtained result in this study, oxalic acid was not able be detected in the work of Kaneco et al. [45], in which the electrochemical reduction of CO$_2$ was under KOH-methanol electrolyte and Ag cathode. The reason can be attributed to the low water content of electrolyte [46,47]. In addition, the obtained results also differ considerably from the report [48], in which the formic acid was the major liquid product under the CO$_2$ reduction using the metal electrode in KHCO$_3$ electrolyte. Therefore, the selectivity of by-products in CO$_2$ reduction process is dominated by not only the electrode materials but also the electrolyte properties. Based on the results, KHCO$_3$ supporting electrolyte possesses better selectivity to convert CO$_2$ to oxalic acid as compared with the electrolyte of Na$_2$SO$_4$.

4. Conclusions

The carbon nanotubes have been successfully grown on carbon fiber by chemical vapor deposition method and used as anode and cathode for MB degradation and CO$_2$ reduction. FTIR spectra indicated that C$_x$H$_y$ functional groups on the CNTs/CF move towards strong stretching vibration as compared with pristine CF. The magnitude of the applied current possessed a greater impact than the type of electrolyte for the degradation of MB in the anodic cell. The maximum degradation efficiency was obtained at optimum applied current of 50 mA, which can promote the high enough production of oxidant but also avoid electrode damage. In the cathodic cell for CO$_2$ reduction, CO and H$_2$ were the main gaseous products while oxalic acid was the liquid product. Hydrogen evolution reaction is predominant at the initial stage of the reaction while CO formation increased significantly at the later stage. KHCO$_3$ supporting electrolyte was recorded to be favorable to both CO formation and hydrogen generation. Furthermore, the sorts of electrodes and
electrolytes were demonstrated to have significant effects on products generated. The developed electrode combined with the electrochemical systems is the priming candidate for the simultaneous electrochemical oxidation of MB and reduction of CO₂ to yield clean energy of H₂ and CO.
Declarations

1. Availability of data and materials

Not applicable.

All figures and table of this manuscript are original and are created by authors.

2. Competing interests

The authors declare that we have no competing interests.

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4. Authors’ contributions

Yu-Ting Yang was responsible for electrodes fabrication and some figures generation. Nhat Huy Luan conducted the materials characterization, MB electro-oxidation and CO$_2$ electro-reduction, and was the major contributor for preparing the manuscript. Dr. Chiung-Fen Chang kindly participated in the discussion of manuscript content and manuscript writing. All authors read and approved the final manuscript.
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