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A new solution route for the synthesis of CuFeO₂ and Mg-doped CuFeO₂ as catalysts for dye degradation and CO₂ conversion



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ABSTRACT

In this study, CuFeO₂ and Mg-doped CuFeO₂ powders are synthesized by using a novel chemical solution route under an ambient atmosphere. By regulating the pH of the reaction solution, on the basis of Pourbaix diagrams, and the stoichiometric ratio of copper to iron ions, delafossite CuFeO₂ powders are formed at 363 K in an aqueous solution. Mg-doped CuFeO2 powders are also synthesized by using the same chemical route with the trace addition of Mg(II) ions. From the powder X-ray diffraction results, all diffraction peaks are of the delafossite structure with dominated 3R phase and few 2H phase. X-ray photoelectron spectroscopy measurements show that the chemical environments of the Cu and Fe ions are consistent with the binding energies of Cu(I) and Fe(III) in the delafossite structure of CuFeO₂. The UV -vis spectra show that the CuFeO₂ and Mg-doped CuFeO₂ powders are both able to absorb light with wavelengths ranging from 300 to 700 nm. The calculated optical band gaps of the CuFeO2 and Mg-doped CuFeO₂ powders are 1.35 and 1.5 eV, respectively. With regard to the application of the powders in the photodegradation of 50 ppm methylene blue, the results suggest that at an incident light irradiation of AM 1.5G, the photodegradation efficiency of the Mg-doped CuFeO₂ powder is remarkably better than that of the CuFeO₂ powder, which can be attributed to its higher carrier concentration. Furthermore, at an external bias of -1.2 V, these delafossite catalysts are able to convert CO₂ to ethylene glycol through an electrocatalytic reaction.

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1. Introduction

Delafossite compounds are well-known transparent conductive materials. Delafossite is often used as a cathode material in photochemical devices to produce hydrogen gas by splitting water. It can also be used as a high-efficiency hole transporting layer in organic photovoltaic devices, in the photocatalytic degradation of dyes or as a phosphor [1–6]. Delafossite consists of a ternary oxide system, with a general formula of $A^+B^{3+}O_2$, where A^+ is a monovalent metal cation such as Cu^+ , Ag^+ , Pd^+ , etc., while B^{3+} is a trivalent metal ion such as Al^{3+} , Ga^{3+} , Cr^{3+} , Fe^{3+} , etc. The atomic structure of delafossite consists

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of a 3R rhombohedral and a 2H hexagonal structure [7]. Intrinsic ptype CuFeO₂ material is one of the delafossite-type semiconductors. With an optical bandgap of approximately 1.32 eV, its absorption range includes the visible light and ultraviolet (UV) spectra. The chemical stability of CuFeO₂ is better than that of a Cu₂O semiconductor, which also has a cuprous ion (cuprous ion is a copper ion with a +1 charge) and readily oxidizes to cupric oxide (CuO) under ambient conditions. Hence, CuFeO₂ has a wider scope of potential applications. Previous studies have mentioned that the positive flat band potential and chemical stability of CuFeO₂ is due to its narrow band gap, which undergoes M²⁺ reduction and H₂ evolution under an incident visible light [8]. In addition, p-type CuFeO₂ can be used as a photocatalyst in the photoinduced reduction of water to produce hydrogen gas in S₂O₂²⁻ aqueous solutions [9].

CuFeO₂ can be synthesized through various methods such as a solid state reaction, a glycine-nitrate process (GNP), a sol-gel reaction, and a hydrothermal reaction. In a solid state reaction, CuFeO₂ is



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formed at a temperature of 900–1200 °C under the presence of nitrogen or argon gas [10-12]. A GNP involves a homogeneous mixing of the reactants and the subsequent heating of the mixture to 200 °C, allowing it to ignite spontaneously and form the products of the reaction. The precursors for the sol-gel method are mostly formed at room temperature, which are then annealed at high temperatures to form CuFeO₂ [13.14]. Lastly, in hydrothermal synthesis, the temperature of the reaction is decreased to 100–280 °C by applying high pressures, thus allowing us to obtain 3R- and 2H-CuFeO₂ powders with an average particle diameter of 100-300 nm [15,16]. A novel synthesis route was discovered by using chemical precipitation method and subsequent ageing the sample in a sealed bottle, which obviously reduced the reaction temperature to 70 °C [17-19]. In short, the existing methods for CuFeO₂ synthesis require high temperatures to promote the diffusion of ions, or require heated aqueous solutions at high pressures. Due to the high temperature requirements of these synthesis methods, defects often appear in the resultant lattice structures and cause electron-hole recombination, which is not ideal for hydrogen production through water splitting with photocathodes [20].

In order to enhance the photoconductivity and incident photonto-current efficiency of CuFeO2, researchers have recently increased the carrier concentrations of Ca^{2+} and Mg^{2+} ions by doping, thus enhancing the photocatalytic efficiency of CuFeO₂ materials. At present, methods for synthesizing metal-doped CuFeO₂ include solidstate reactions [21–23], sol-gel reactions [24,25], and hydrothermal methods [26]. When Mg²⁺ ions enter the structure of CuFeO₂, two substitution modes will occur. The Mg²⁺ ions will substitute in the sites of Fe³⁺ ions, which results in an electron deficiency and an electron hole. Furthermore, after entering the interstitial sites in the copper layer, the Mg²⁺ ions will displace three Cu⁺ ions, which leaves sufficient space to accommodate the Mg²⁺ions. This also results in three copper ion vacancies, an interstitial ion and electron holes. Hence, the conductivity of the material is enhanced as the number of electron holes in both substitution methods [22]. When Mg²⁺ ions substitute Fe³⁺ ions, a superlattice is also formed at the interface between the Cu conductive layer and the octahedral FeO₆ nonconductive layer in the structure. As a result, the physical properties and the band structure of the material are significantly altered.

This study is devoted to the discovery of a new chemical solution method to synthesize CuFeO2 and Mg-doped CuFeO2 powders via one-step chemical precipitation method. CuFeO₂ powder in the 3R and 2H phases is synthesized at atmospheric pressure and at 90 °C by modifying the mole ratio of cupric and ferrous ions, and by adjusting the pH of the reaction solution. The same synthesis process is also successfully used to prepare Mg-doped CuFeO2 powder. A chemical solution deposition is carried out in the liquid phase. Prior to deposition, the metal ions are sufficiently mixed in the solution. When the pH of the solution is increased, the M - OH species undergoes dehydration, leading to the formation of a solid powder. Therefore, the synthesis process requires a relatively low temperature and takes place at ambient conditions. This process is also called forced hydrolysis. In terms of application, a preliminary study was performed on the photocatalytic degradation of dye and the CO₂ conversion to organic compound of the synthesized CuFeO2 material, so as to evaluate its potential in practical applications.

2. Material and methods

2.1. Synthesis of CuFeO₂ and Mg-doped CuFeO₂

In the experiments of this study, $CuFeO_2$ powder was synthesized through chemical solution synthesis. A solution with a pH of 2 was formed by adding 0.19 mL of HCl (36.5%, J. T. Baker) to 200 mL of deionized (D.I.) water. The solution was placed on a hot plate and

heated to 90 °C. Then, 0.363 g of Cu(CO₂CH₃)₂ (98%, Sigma Aldrich) and 0.723 g of FeSO₄ \cdot 7H₂O (97%, Showa) (molar ratio Cu:Fe = 1:1.3) were added into the solution and were stirred homogeneously. 35 mL of 1 M NaOH solution was added immediately as a precipitant. The pH of the solution was adjusted to 12, and the solution was stirred continuously for 6 h at 90 °C. After the reaction, the solid products were separated from the solution through suction filtration. Subsequently, the solids were dried in an oven at 50 °C and grounded into powder. The aforementioned procedure was also used in the synthesis of Mg-doped CuFeO₂. A 200 mL aqueous solution with a pH of 2 was prepared and heated to 90 °C. 0.363 g of Cu(CO₂CH₃)₂, 0.834 g of FeSO₄·7H₂O, and 0.04 mL of 1 M MgCl₂(aq) (98%, Sigma-Aldrich) (molar ratio Cu:Fe:Mg = 1:1.3:0.02) were then successively added into the solution and were stirred homogeneously. 35 mL of 1 M NaOH solution was then quickly added into the solution, and the pH of the solution was adjusted to 12. The solution was then stirred continuously for 12 h at 90 °C. After the reaction, Mg-doped CuFeO₂ powder was obtained through suction filtration, drying, and grinding.

2.2. Photocatalytic degradation of methylene blue

In the experiments, 50 mg of CuFeO₂ and Mg-doped CuFeO₂ powders were used as a photocatalyst. The photodegradation of 50 mL of 50 ppm methylene blue solution (MB) ($C_{16}H_{18}N_3SCl \cdot 3H_2O$, 95%, Acros) was carried out at an incident visible light with an irradiance of AM 1.5 G. Small quantities of MB solution were sampled at different time intervals for UV–vis measurements. Magnetic stirrers were used in all the experiments, so as to prevent the powders in the beakers from precipitating. Prior to the UV–vis measurements, the sample liquids were also centrifuged at a high speed (14,000 rpm) to prevent interference caused by the powders.

2.3. Electrochemical analysis

A mixture of 0.02 g of delafossite powder, 500 μL of D.I. water, and 500 μ L of ethanol was placed into an ultrasonic bath for 30 min to allow homogeneous mixing. 20 μL of the solution was then dripped onto a piece of carbon paper and dried at 70 °C. Meanwhile, 10 µL of 0.1% Nafion (Sigma-Aldrich) was dripped onto a piece of carbon paper containing a catalyst and dried. The product was utilized as a carbon electrode containing 0.4 mg of delafossite powder. Cyclic voltammetry (CV) and amperometry were carried out in a CO₂(g) saturated 0.1 M KHCO₃(aq) solution with a pH of 6.7. Carbon paper, an Ag/AgCl electrode, and Pt wire were used as the working electrode, the reference electrode, and the counter electrode, respectively. CV measurements were carried out at a range of -1.6 to 0.5 V vs Ag/AgCl and at a scan rate of 100 mV/s. The CO₂ conversion experiments were performed for 12 h by applying a bias of -1.2V at the working electrode. After 12 h of electrocatalytic reaction, the products in the solution were identified through ¹H and ¹³C nuclear magnetic resonance spectroscopy (NMR).

2.4. Characterization

The crystalline phases of the samples were analyzed using a powder X-ray diffractometer (XRD; Rigaku DMX-2200). The photodegradation efficiency of the samples were monitored using a UV–vis spectrophotometer (PerkinElmer Lambda 900). The X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo Fisher Scientific K-Alpha spectrometer with Al K α radiation. The ¹H and ¹³C NMR spectra of the CO₂ conversion were analyzed with a Bruker AV-400 NMR instrument.

3. Results and discussion

3.1. Materials analysis

According to the Pourbaix diagram, the iron and copper ions are soluble in acidic H₂O and are able to form iron oxide and copper oxide when the pH of the solution is adjusted to alkaline conditions [27]. In the control experiments, Cu(CO₂CH₃)₂ and FeSO₄·7H₂O compounds were separately added to a solution with a pH of 2, and the pH of the solution was adjusted to 12. As a result, CuO and Fe₂O₃, FeOOH, and Fe₃O₄ powder precipitates were formed, respectively. These products are in line with the phenomena in the Pourbaix diagram, and the X-ray diffraction (XRD) spectra of the products are shown in Fig. S1. This phenomenon indicates that it is possible to precipitate these two metal ions simultaneously in basic solution by regulating the synthesis parameters including the reaction temperature, stoichiometry of the reactants, valence of the metal ions, and pH of the solution. First, at a fixed ratio of the reactants Cu(CO₂CH₃)₂ and FeSO₄·7H₂O, the effects of temperature on the reaction were investigated. When the temperature of the reaction was lower than 80 °C, 3R-CuFeO₂ had already been formed, and this was followed by the formation of FeOOH, Fe₃O₄, and CuO. When the temperature was 90 °C, 3R–CuFeO₂ generated a strong diffraction signal, as evident in the XRD measurements. There were no signals generated by the other products, as shown in Fig. S2. Similarly, the results from multiple experiments show that, at a molar ratio of Cu^{2+} : Fe²⁺ = 1:1.3. reaction time of 6 h. and temperature of 90 °C. the product was determined to be CuFeO2 with 3R (rhombohedral) and 2H (hexagonal) phases, as evident in the XRD measurements. As shown in Fig. 1, the characteristic peaks of 3R-CuFeO₂ appeared at $2\theta = 31.2^{\circ}, 35.7^{\circ}, 40.2^{\circ}, 43.3^{\circ}, 47.7^{\circ}, 55.2^{\circ}, 61.0^{\circ}, 64.8^{\circ}, 65.2^{\circ}, 70.1^{\circ},$ 72.7° , and 75.6° , which corresponded to the planes of (006), (012), (104), (015), (009), (018), (110), (1010), (0012), (0111), (202), and (024) of CuFeO₂, respectively. Even though the diffraction signal of 2H–CuFeO₂ had overlapped with that of 3R–CuFeO₂ at multiple angles, both phases could be distinguished by their characteristic diffraction peaks at $2\theta = 34.5^{\circ}$ (101) and 37.6° (102). While determining the optimal conditions for synthesis, the researchers attempted to adjust the reagent stoichiometry of Cu^{2+}/Fe^{2+} to 1–1.2. However, this would still produce a small amount of CuO, which



Fig. 1. XRD spectra of the synthesized $CuFeO_2$ powder at a $Cu^{2+}:Fe^{2+}$ molar ratio of 1:1.3, reaction temperature of 90 °C, and reaction time of 6 h.

indicates that Cu species precipitate faster than Fe and more Fe ions are needed for simultaneous coprecipitaion.

Based on the results above, Cu^{2+} and Fe^{2+} ions are able to form CuFeO₂ under basic conditions. Cu(CO₂CH₃)₂, instead of CuSO₄, was employed as the copper ion source owing to the chelating capability of the anion, CH₃COO⁻. Chelating ligands were used to moderate the high reactivity of metal species leading to less hydrolysis rate and blocking coordination sites at the metal ions, in oder to reduce the growth rate of metal hydroxide and subsequent metal oxide. In a forced hydrolysis reaction, aqua (H₂O) and hydroxo (OH) ligands bound to metal ions convert to oxo (M = O or M-O-M) when the pH is increased, which indicates that the formation of oxides is favored for high pH. According to the Pourbaix diagram, when the pH of the solution was adjusted from 2 to 12, the metal ions would first form metal hydroxides, followed by metal oxides. Furthermore, pH of 12 is the highest basic ambiance that Cu₂O can sustain. When the coprecipitation reaction is carried out, two reactants must precipitate simultaneously in order to form binary metal oxide compounds. In the system utilized in this study, a spontaneous redox reaction occurred during the precipitation process ($Cu_2O + Fe_2O_3 = 2CuFeO_2$), as shown in the following reactions [28]:

 $2Fe(OH)_2 + 2OH^- \rightarrow Fe_2O_3 + 3H_2O + 2e^- E^0 = 0.86 \text{ V}$ (1)

$$2Cu(OH)_2 + 2e^- \rightarrow Cu_2O + 2OH^- + H_2O E^0 = -0.08 V$$
 (2)

 $2Cu(OH)_2 + 2Fe(OH)_2 \rightarrow Cu_2O + Fe_2O_3 + 4H_2O E = 0.78 V$ (3)

In addition to the multitude of factors influencing the reaction, the researchers also attempted to add excess chelating agents, e.g. CH₃COOH and ethylenediamine, into the reaction solution. The results, however, did not improve. Due to the difference in the rate of precipitation of Cu^{2+} and Fe^{2+} ions, CuO was formed when the molar ratio of the reactants was Cu^{2+} :Fe²⁺ = 1:1, as proven in the XRD measurements (Fig. S3). This was also the reason for adding 30% more Fe²⁺ ions in the mixture. As shown in Fig. S4, delafossite can be formed at the reaction temperature of 60 °C in the liquid phase accompanied by the formation of a few CuO. Since the attachment of the reaction generated species is weak, it allows the species to redissolve and attach to the surface in a position required for a crystalline structure of delafossite by increasing the reaction time and temperature at pH = 12. As shown in Fig. S5, delafossite was formed at the reaction time of 2h and the pure phase was acheived by increasing the reaction time. The method herein facilitates the synthesis procedure and is suitable for use in the production of large-scale delafossite powders without using aging process or hydrothermal equipments.

Previous experiments have shown that when the molar ratio of $Cu(CO_2CH_3)_2$ and $FeSO_4 \cdot 7H_2O$ is 1:1.3, $CuFeO_2$ with a purer phase can be prepared at a temperature of 90 °C and a reaction time of 6 h. Hence, these parameters were utilized in the Mg^{2+} doping reaction. When the stoichiometry ratio of the reactants was $Cu^{2+}:Fe^{2+}:Mg^{2+} = 1:1.3:0.02$, even though $CuFeO_2$ in the 3R phase had formed after 6 h of reaction, the reaction also yielded Cu_2O , whereas after 12 h of reaction, Mg-doped $CuFeO_2$ could be synthesized, as shown in Fig. 2. Since trace amounts of Mg^{2+} doping would not overtly alter the crystalline phase of $CuFeO_2$ [22], the generated diffraction patterns were similar to the $CuFeO_2$ diffraction patterns (JCPDF 39–0246). The characteristic peaks appeared at $2\theta = 31.2^{\circ}$, 34.5° , 35.7° , 40.2° , 43.3° , 47.6° , 55.2° , 61.0° , 64.8° , 70.1° , 72.7° , and 75.6° , which corresponded to the planes of 3R–CuFeO₂ of (006), (101), (012), (104), (015), (009), (018), (110), (1010), (0111), (202), and (024), respectively.

XPS was used to analyze the composition of the products further, and photoelectrons of Cu, Fe, and O were observed on the surface of CuFeO₂. The high resolution spectra of the O 1s, Fe 2p, and Cu 2p are shown in Fig. 3a–c. The binding energy of the O 1s electrons was at



Fig. 2. XRD spectra of the synthesized Mg doped-CuFeO₂ powder at a Cu²⁺:Fe²⁺:Mg²⁺ molar ratio of 1:1.3:0.02, reaction temperature of 90 $^{\circ}$ C, and reaction time of 12 h.

ca. 530 eV, which is typical for an oxide surface. In Fig. 3b, the 710.2 and 723.6 eV signals correspond to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ electrons, respectively, which conforms to the binding energy of Fe^{3+} in CuFeO₂. In Fig. 3c, the signals at 951.6 and 931.8 eV are respectively determined to be those of $Cu^+ 2p_{1/2}$ and $Cu^+ 2p_{3/2}$ electrons. A weak peak satellite at 944 eV is also observed. Shoulder peaks are also observed at the binding energies of 953.6 eV and 933.6 eV, which indicates that cupric ions (Cu^{2+}) are still present in the products and could be formed through oxidation at humid conditions [29]. The quantity of the Cu⁺:Cu²⁺ was estimated from the integration of the signal area, and the ratio was 1:0.32. Fig. 3d-f shows the highresolution XPS spectra of O 1s, Fe 2p, and Cu 2p electrons on the surface of Mg-doped CuFeO₂, which shows the similar chemical environments of O, Fe, and Cu atoms in CuFeO₂ and Mg-doped CuFeO₂. Moreover, by integrating the area in curve-fitting, the ratio of Cu⁺:Cu²⁺ was estimated to be 1:0.42. The higher concentration of Cu^{2+} may attributed to the doping process, during which Mg^{2+} ions entered the copper layer and displaced the Cu⁺ ions. In addition, the Cu⁺ ions readily oxidized into Cu²⁺ on the surface of the sample, which resulted in higher amounts of Cu²⁺ ions on the surface of the Mg-doped CuFeO₂ sample [22]. Even though all the signals confirmed the presence of cuprous ions and ferric ions in the product, there was still a small amount of cupric ions.

Since the concentration of magnesium ions in the powder was below the detection limit of the instrument, Mg 1s electrons were not detected at a binding energy of 1303 eV in the XPS measurement [30]. In order to determine if Mg²⁺ ions had been successfully doped into the CuFeO₂ material, ICE-AES was used to conduct a quantitative analysis of the sample. The results indicated that the atomic ratio of Cu:Fe:Mg was 1:1.3:0.02, which was the same as the stoichiometric ratio of the reactants. These results suggest that the liquid phase synthesis method developed in this study is able to successfully and homogeneously distribute all three metal ions in the product, and is also applicable when doping trace amounts of metal elements. Even though an excess of Fe²⁺ ions was added during synthesis, the diffraction signal of iron oxide was not detected in the XRD measurements, which could be a result of the amorphous or low degree of crystallinity of the iron oxide formed in the reaction.

The absorption spectra of copper delafossite particles were measured in the wavelength range of 300-1000 nm, as shown in Fig. 4a. Both the CuFeO₂ and Mg-doped CuFeO₂ showed absorption in the wavelength range of 300-700 nm, and a decrease in absorption could be seen at wavelengths longer than 700 nm. The range of

absorption of both samples included UV light and visible light. The optical bandgaps are estimated by the following equation:

$$(\mathbf{a}\mathbf{h}\boldsymbol{v})^{1/n} = \mathbf{A}(\mathbf{h}\boldsymbol{v} - \mathbf{E}_{\mathbf{g}}) \tag{4}$$

where α , h, v, n, A, and E_g are the absorption coefficient, Planck constant, the frequency of light, power factor, a constant, and the band gap, respectively. The bandgap energy can be calculated through linear extrapolation by plotting the graph of $(\alpha h v)^{1/n}$ v.

s. *hv*. UV–vis measurements are used to measure the optical reflectance spectrum of CuFeO₂, and n = 1/2 is employed to calculate the direct optical band gap of CuFeO₂. Fig. 4b shows that the band gap of CuFeO₂ was 1.35 eV, which conforms to its theoretical value [31,32]. This value, however, is much higher than the experimental value of 1.15 eV [33]. This may be due to the excessive 30% iron oxide (Fe₂O₃ E_g = ~2.2 eV) remaining in the sample, which increased the optical band gap of the product [34,35]. According to Fig. 4c, the band gap of the Mg-doped CuFeO₂ powder was 1.5 eV. In addition to the excessive iron oxide in the sample, after entering the CuFeO₂ material, Mg²⁺ ions would increase the p-type carrier concentration, which would lead to the Burstein-Moss effect, thereby increasing the optical band gap [23,24].

3.2. Photocatalytic degradation

Copper oxides and Cu(I) delafossite materials are considered to have good catalytic properties to degrade organic dye molecules [36–40]. In this study, MO was degraded in order to observe the degradation efficiency of the photocatalysis. Methylene blue (MB) solution was degraded in the experiments, in which 0.05 g of CuFeO₂ and Mg-doped CuFeO₂ were used as catalysts. Both photocatalytic degradation of dye tests were carried out separately under an AM 1.5 G visible light source. AUV-vis spectrometer is used to analyze the spectra at a wavelength range of 400-800 nm. The degradation efficiency was recorded and compared at $\lambda = 650$ nm, corresponding to the highest absorption wavelength of MB. According to Fig. 5a, the degradation efficiency of 50 ppm MB by the CuFeO₂ powder at photocatalytic reaction times of 15 and 60 min was 55.6% and 57.0%, respectively, based on the concentration ratio C/C₀ of MB solution. On the other hand, the degradation of MB by the Mg-doped CuFeO₂ powder increased with the time of visible light illumination. The degradation efficiency of the dye was 83.3% after 15 min, and was further increased to 92.7% after 90 min, as shown in Fig. 5b. These results suggest that both powders are able to effectively degrade MB, and also that the Mg-doped CuFeO2 powder possesses excellent photodegradation efficiency. This can be explained by the occurrence of two substitution forms after the addition of magnesium, i.e. CuFe₁₋ _xMg_xO₂ and Cu_{1-3x}Mg_xFeO₂. Mg displaces Fe in the former, while Mg displaces Cu in the latter. However, an excess doping of Mg or Cu deficiency will increase the impurity concentration, which lowers its photoresponse and carrier mobility. An appropriate dopant amount, e.g. 0.02 mol% in this study, possesses a higher carrier concentration for dye degradation.

3.3. CO₂ conversion

Owing to its relatively small band gap, p-type conductivity, and conduction band edge higher than CO_2 reduction potentials, delafossite CuFeO₂ has emerged as a promising material to drive CO_2 reduction [41–45]. In this study, the CV technique was used to analyze the electron transfer behavior using two delafossite materials as the working electrodes. Fig. 6 shows the cyclic voltammograms (CV) of the CuFeO₂ and Mg-doped CuFeO₂ powders after ten oxidation-reduction cycles. As shown in the figures, two



Fig. 3. High-resolution XPS spectra of the (a) O 1s, (b) Fe 2p, and (c) Cu 2p electrons of CuFeO2 and the (d) O 1s, (e) Fe 2p, and (f) Cu 2p electrons of Mg-doped CuFeO2.

oxidation peaks were observed at potentials of 0 and 0.6 V v.s. RHE, while a reduction peak was seen at a potential of 0.3 V vs. RHE. This could be attributed to the oxidation-reduction reaction of copper ions [46]. Another reduction peak could be seen at a potential of -0.5 V vs. RHE. This can be attributed to the reduction of CO₂. Fig. 6a and b also show that both the oxidation and reduction currents measured for the CuFeO₂ electrodes were greater than

those for the Mg-doped CuFeO₂ electrode. Furthermore, the current values of the oxidation-reduction peaks gradually decreased in the 1st to 5th CV cycles, and a slight shift had occurred in the potentials. In the 6th to 10th CV cycles, the oxidation-reduction current values of the copper ions and their potentials gradually became consistent, which indicates the disintegration of the electrode materials in the electroanalysis process.



Fig. 4. (a) UV-vis absorption spectra of CuFeO2 and Mg-doped CuFeO2, and calculated bandgap energy of (b) CuFeO2 and (c) Mg-doped CuFeO2.



Fig. 5. UV–Vis absorption spectra of MB (50 ppm) degradation efficiency tests using (a) CuFeO₂ and (b) Mg-doped CuFeO₂ powders as the photocatalyst under AM 1.5G exposure.

On the basis of the MB degradation results, Mg-doped CuFeO₂ possesses higher carrier concentration and higher catalytic characteristics than CuFeO₂. However, at an external bias of $0.5 \sim -1.6$ V, the CV measurements suggest a higher oxidation-reduction potential of the CuFeO₂ material. When magnesium ions enter the CuFeO₂ lattice prepared at 363K without high temperature sintering, they will disturb the atomic arrangement, and its structure is

further damaged when an external bias is applied during electroanalysis. As shown in cycles 1 to 4 in Fig. 6b, the current value decreases when the number of scans performed increases.

The product obtained after applying a bias of -1.2 V on the working electrode in a CO₂ saturated 0.1 M KHCO₃(aq) solution at pH = 6.7 for 12 h was subjected to a ¹H and ¹³C NMR analysis. The measurement sample was prepared by mixing 585 µL of electrolyte solution at the cathode with 1.3 µL of DMSO. In the ¹H spectrum (Fig. 7), the chemical shifts at 4.79 and 2.73 ppm corresponded to the proton in H₂O and DMSO, respectively. The chemical shift at 3.67 ppm in the ¹H spectrum (Fig. S10) confirmed that CO₂ converts to ethylene glycol via electrocatalytic reaction using CuFeO₂ as the catalyst [47]. DMSO was added as an internal standard for quantitative purposes. The yield of the reaction can be calculated through the following equation.

$$\frac{DMSOmol}{EGmol} = \frac{6/Peak Area}{4/Peak Area}$$
(5)

in which 6 and 4 respectively represent the number of protons in a DMSO and EG molecule in ¹H NMR, while *Peak Area* represents the NMR peak area. Hence, the quantity of EG in the NMR tube can be calculated. The results show that after 12 h of electrocatalysis, the CuFeO₂ powder yielded 1.8281×10^{-3} g of EG, while the Mg-doped CuFeO₂ powder yielded 1.585×10^{-3} g of EG. These results conform to the CV measurements. When an external bias is applied, the tiny structural damages caused by magnesium ion doping are not ideal for the application of delafossite materials in liquid phase catalytic



Fig. 6. Cyclic voltammograms of (a) the CuFeO₂ and (b) the Mg-doped CuFeO₂ containing carbon electrode in 0.1 M $KHCO_3(aq)$ solution at pH = 6.7.



Fig. 7. ¹H NMR spectra of CO₂ conversion products using (a) CuFeO₂ and (b) Mg-doped CuFeO₂ powders as the catalyst.

reactions. Interestingly, there are no reports of the capability of CO_2 to be converted into EG, and its mechanisms have not been delineated. In previous studies where CO_2 was reduced to methanol and ethanol through electrochemical methods, the production of hydrogen and the reduction of CO_2 were indicated as competitive reactions, as the hydrogen produced in the aqueous solution will react with the carbonate ions in water to form organic compounds [48,49]. C–C bond coupling during CO_2 conversion has been discovered in a photoelectrochemical reduction using Fe–Cu oxide as the catalyst, leading to the formation of acetate [44]. It is speculated that the formation of EG is similar to the aforementioned reaction route.

4. Conclusions

A novel chemical solution route for the synthesis of $CuFeO_2$ and Mg-doped $CuFeO_2$ powders at atmospheric pressure and at a temperature of 90 °C is proposed in this study. The optimization of conditions at atmospheric pressure and low temperatures is determined for the synthesis process, which usually requires high temperatures or high pressures. Chemical analyses confirmed the products as $CuFeO_2$ and Mg-doped $CuFeO_2$, which contain an excess amount of iron oxide. Even though the authors had previously attempted to control the rate of precipitation of the copper and iron by adjusting various synthesis parameters, such as the stoichiometric ratio of the reactants, temperature of the results had not surpassed those reported in this study. This suggests that substantial challenges persist in the synthesis of delafossite materials at

atmospheric pressure and low temperatures. In terms of the application of materials, the delafossite material synthesized was proven to have a high degradation efficiency in degrading dyes. Interestingly, the CuFeO₂ powder was able to yield a higher quantity of EG in a CO₂ saturated KHCO₃(aq) solution than the Mg-doped CuFeO₂ powder. It is speculated that this was caused by the reduced stability of the CuFeO₂ material through an electrochemical reaction that occurs when the magnesium ions enter the CuFeO₂ lattice. This phenomenon was also observed in the CV measurements.

CRediT authorship contribution statement

Yu-Hsu Chang: Conceptualization, Methodology, Validation, Writing - original draft, Supervision, Writing - review & editing. Haicheng Wang: Conceptualization, Methodology, Validation, Writing - review & editing. Ting-Fong Siao: Writing - original draft, Formal analysis, Investigation. Yuan-Han Lee: Writing - original draft, Formal analysis, Investigation. Shi-Yun Bai: Formal analysis, Investigation. Ching-Wen Liao: Formal analysis, Investigation. Jie-Kai Zhuang: Formal analysis, Investigation. Te-Wei Chiu: Conceptualization. Chun-Hong Kuo: Conceptualization, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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