**Carbon based copper(II) phthalocyanine catalysts for electrochemical CO2 reduction: Effect of carbon support on electrocatalytic activity**

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**Abstract**

Carbon-metal hybrid materials have shown promising performance as electrocatalysts for CO2 reduction. Here, a comparative study of how different carbons supports can influence this reaction is presented. The tested carbon supports were graphene oxide, multi-walled carbon nanotubes, carbon black and activated carbon while the metal complex selected was copper(II) phthalocyanine (CuPc). CuPc supported on carbon nanotubes and carbon black were found to give higher faradaic efficiencies for reduced carbon products compared to graphene oxide and activated carbon. This is likely due to lower charge transfer resistances observed for carbon nanotubes and carbon black, owing to graphitic structures present. Amongst various sizes of carbon nanotubes, long and thin tubes (in the range of 10-30 nm diameter size and 10-30 µm length) demonstrated higher faradaic efficiencies to carbon products relative to shorter and thicker ones. This could possibly be explained by differences in surface area. Additionally, the novel use of carbon nanotubes synthesized from post-consumer plastic waste was also explored as a potential carbon support material. It demonstrated comparable performance to commercial carbon nanotubes in terms of faradaic efficiencies to reduced carbon products.

**Keywords**

Carbon nanotube, carbon black, copper(II) phthalocyanine, CO2 reduction

**1. Introduction**

Electrochemical CO2 reduction has gained scientific interest as it offers mitigation of the greenhouse gas and at the same time facilitate production of valuable chemicals, thus directly addressing increasing global warming. Furthermore, this technology can be powered with clean energy from renewable sources, i.e. solar and wind, thus making it a sustainable solution with near zero operational carbon footprint. However, there are many technical barriers hindering its economic viability and one of the key areas for improvement is on the development of more energy efficient and cost effective electrocatalysts [[[1]](#endnote-1)].

In fact, many metals and their complexes were found to be electrocatalytically active towards reduction of carbon dioxide, e.g. copper, silver, tin and bismuth [[[2]](#endnote-2)-[[3]](#endnote-3)[[4]](#endnote-4)[[5]](#endnote-5)[[6]](#endnote-6)]. To further increase their catalytic performance of metals, various types of carbon supports were introduced. These carbon supports included graphene oxide, carbon nanotubes, carbon black and activated carbon [1,11,[[7]](#endnote-7)-[[8]](#endnote-8)[[9]](#endnote-9)[[10]](#endnote-10)]. This hybridization strategy combined the high electrocatalytic performance of metals, as well as the large surface area and good stability of carbon support [1,[[11]](#endnote-11)]. Similar strategy had also been adopted for the design of electrocatalyst for other reactions, namely hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) [[[12]](#endnote-12)-[[13]](#endnote-13)[[14]](#endnote-14)[[15]](#endnote-15)].

In the area of electroreduction of CO2, there have been some attempts to alter the type of carbon support to optimize its catalytic performance [[[16]](#endnote-16),20]. In this study, an attempt to explore this matter to facilitate the development of electrocatalysts for CO2 reduction via application of various carbon supports was made. As carbon supports, representative materials of different carbon structural groups such as graphene oxide, activated charcoal, carbon nanotubes and carbon black were selected [7,10,[[17]](#endnote-17)-[[18]](#endnote-18)]. Furthermore, phthalocyanines were found to be effective metal clusters for preparation of CO2 electrocatalysts [[[19]](#endnote-19)-[[20]](#endnote-20)[[21]](#endnote-21)[[22]](#endnote-22)[[23]](#endnote-23)]. Amidst various metals, copper was selected as it is the only metal known of producing valuable C2 or higher carbon products (such as ethylene and ethanol) from the electrochemical reduction of carbon dioxide [4,[[24]](#endnote-24)]. Besides that, different sizes of carbon nanotubes as well as the possibility of using waste derived carbon nanotubes as carbon supports was also investigated. To the best of our knowledge, these studies have not been reported yet and the findings would be insightful when considering carbon supports to use for metal-carbon based electrocatalysts for CO2 reduction.

**2. Results and discussion**

*2.1. Material characterization*

Although each of electrocatalyst’s supports was carbon-based, the properties of carbon can vary significantly depending on the synthesis method, which can subsequently affect the properties of the final product. For instance, graphene oxide is typically prepared by using strong oxidizing agents on graphite [[[25]](#endnote-25),[[26]](#endnote-26)] while activated carbon is mainly synthesized through pyrolysis of carbonaceous materials at temperatures below 1000 oC [[[27]](#endnote-27)]. On the other hand, carbon nanotubes are often made through chemical vapor deposition (CVD) process at temperatures below 1200 oC [[[28]](#endnote-28)]. Furthermore, carbon black is produced by pyrolysis of carbonaceous industrial waste (e.g. oil cokes, residual oil) using high temperature flame (up to 2000 oC) [[[29]](#endnote-29)]. These synthesis processes result in the carbon material with different morphologies, chemical functionalities, crystallinity and surface area. There are various types of graphene oxide, activated carbon, carbon nanotubes and carbon black, which makes comparison of supports even more challenging. For selection of representative types of carbon supports, materials with proven electrochemical activity were chosen. For example, among the different oxidation methods for making graphene oxide, one synthesized by Hummers method was selected [[[30]](#endnote-30),[[31]](#endnote-31),[[32]](#endnote-32)[[33]](#endnote-33)]. Among activated carbons, one derived from charcoal was chosen [[[34]](#endnote-34)]. In the case of carbon nanotubes, thin and long nanotubes (10-30 nm diameter and several micrometer in length) were selected [18,[[35]](#endnote-35),[[36]](#endnote-36)]. For carbon black, Vulcan XC72 (from Cabot) was used as it is characterized with high conductivity [[[37]](#endnote-37)]. As such, it is important to provide adequate material characterization of the carbon supports. The field-emission scanning electron microscopy (FESEM), Fourier Transform Infrared Resonance (FTIR) spectroscopy and X-ray diffraction (XRD) characterization of the carbon supports are provided in the supporting information (SI) Fig. S1-S3.

The hybridized metal-carbon materials were synthesized in accordance with a previous report [20]. Basically, different carbon supports were dispersed in dimethyl formamide (DMF), sonicated with CuPc followed by an overnight stirring at room temperature. The solids were then collected and washed with DMF and ethanol. The synthesized materials were named in accordance with the carbon support used, i.e. graphene oxide- CuPc, activated carbon- CuPc, carbon nanotube- CuPc and carbon black- CuPc. To ascertain the synthesis process, the FESEM and the X-ray energy dispersive spectroscopy (EDS) were conducted on the prepared materials. The FESEM-EDS images showed an even distribution of Cu over the carbon supports (Fig. 1). In comparison with the FESEM images of carbon supports before modification (Fig. S1), rod-like structures of CuPc were seen coated on the surfaces of the carbon after hybridization. This was likely due to excess amount of CuPc used during synthesis [20].

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**Fig. 1.** SEM imaging (left column) and corresponding Cu elemental mapping from EDS (right column, Cu represented in yellow) for various carbon supported copper(II) phthalocyanine, (CuPc).

The FTIR results further verified the successful synthesis of the carbon-metal hybrids, with presence of CuPc detected in the materials in the fingerprint region between 400 and 1600 cm-1 (Fig. 2). In the unmodified carbon supports, small quantities of C=O (~1640-1720 cm-1) were observed in their FTIR spectra (Fig. S2). These peaks appeared to remain present after hybridization, suggesting that CuPc does not form covalent bonding with the carbon support supports via the C=O functional group.



**Fig. 2.** FTIR analysis of hybridized carbon-metal materials and copper(II) phthalocyanine.

Transmission electron microscopy (TEM) images indicated that the morphologies remain unchanged after hybridization (Fig. 3). Wrinkled structures of graphene oxide can still be seen while activated carbon showed thick structures. Meanwhile, multi-walled carbon nanotubes had tube-like structures while carbon black showed spherical-like structures. A size distribution analysis of the carbon-metal hybrids was performed from at least a hundred samples from TEM imaging and presented in Fig. 4.



**Fig. 3.** TEM images of various carbon supported CuPc after synthesis.



**Fig. 4.** Size analysis of various carbon supported CuPc obtained from TEM analysis of at least 100 samples.

Besides that, the materials were also characterized by the X-ray photoelectron spectroscopy (XPS) to probe the chemical moieties present on their surfaces (Fig. 5). The wide survey scan indicated presence of Cu 2p and N 1s peaks confirming the successful introduction of CuPc onto all carbon supports. Traces of Al and Si impurities were observed, possibly introduced from the CuPc starting material (Al 2p ~75 eV, Si 2p ~100 eV). The Ni and Mn impurities, which could influence the electrocatalytic properties of carbon materials, were not detected from XPS measurement [[[38]](#endnote-38),[[39]](#endnote-39)]. As the Cu content was much higher than other metals in the sample, the effect of trace metals was likely to be negligible in this study. Meanwhile from the XPS high resolution Cu 2p spectra, Cu 2p 1/2 and Cu 2p 3/2 and their satellite peaks can be seen at c.a. 955 eV and 935 eV respectively indicating the presence of Cu2+ from CuPc [[[40]](#endnote-40),[[41]](#endnote-41)]. A slight shift could be observed for Cu2+ 2p 3/2 peak towards lower binding energy for the composite materials relative to CuPc (ranging between 0.1 to 0.6 eV). These small shifts suggested a non-covalent intercalation or adsorption between CuPc with the carbon supports [[[42]](#endnote-42),[[43]](#endnote-43)].In the case of carbon black-CuPc, an additional peak was seen at lower binding energy (~933 eV) possibly due to the reduction of Cu2+ to Cu+ phase [[[44]](#endnote-44)].

**Fig. 5.** XPS spectra of different carbon supported copper(II) phthalocyanines: (A) wide survey scan, and (B) high resolution Cu 2p scan.

The copper content in the carbon-metal hybrid materials was determined using acid microwave digestion and the ICP-OES. Their Cu content was found to be relatively similar in all electrocatalysts (ca. 5-8 wt %, see SI, Table S1).

*2.2. Electrochemical studies between different carbon materials supported CuPc*

After material characterization, detailed electrochemical studies were conducted (Fig. 6). Cyclic voltammetry (CV) measurements were carried out under CO2- and N2-saturated 0.5 M KCl solutions. The pH values of these solutions are available in the SI (Table S2). A KCl solution was chosen as it was proven to inhibit the competing hydrogen evolution reaction (HER) [[[45]](#endnote-45)]. As presented in Fig. 6A, the cathodic current in CO2-saturated solution is generally lower or similar to that obtained in N2-saturated solution. This trend is consistent with previous studies where KCl solution was used as the electrolyte [7,45]. Amongst the prepared catalysts, carbon nanotube-CuPc showed the highest current density (-23.7 mA/cm2) at -1.8 V vs Ag/AgCl, followed by carbon black-CuPc (-5.9 mA/cm2), activated carbon-CuPc (-3.0 mA/cm2) and graphene oxide-CuPc (-1.6 mA/cm2).

To characterize the products upon CO2 reduction, chronoamperometry measurements were conducted for 1 h in CO2-saturated 0.5 M KCl solution at -1.05 V versus the reversible hydrogen electrode (RHE). This potential was chosen as it is equivalent to -1.6 V versus Ag/AgCl where products start to form as seen from the increase in negative current observed from the CV curves. The chronoamperograms (Fig. 6B) display a similar trend of current densities to that seen from CV results (carbon nanotube-CuPc > carbon black-CuPc > activated carbon-CuPc > graphene oxide-CuPc). In terms of product formation, graphene oxide-CuPc and activated carbon-CuPc mainly generated hydrogen gas with Faradaic Efficiency () above 75% (refer to Table 1). There could be some traces of other products produced by graphene oxide-CuPc that were below the limit of detection of the equipment used, as its total faradaic efficiency was lower than 100%. In contrast, the carbon nanotube-CuPc and the carbon black-CuPc formed a wider range of products including methane, ethylene and formic acid. Interestingly, in the case of carbon black-CuPc, ethanol was additionally formed (FEethanol = 15%) even though its total current density (c.a. -4 mA/cm2) was lower than that of the carbon nanotube-CuPc (c.a. -5 mA/cm2). In terms of generating CO2 reduced products (i.e. CO, formic acid, methane, ethylene, ethanol), their sum of faradaic efficiency values for carbon nanotube-CuPc amounted to 66.3%, while for carbon black-CuPc, it was 81.8%. This is likely a result of higher hydrogen production observed for the carbon nanotube-CuPc compared to the carbon black-CuPc. A possible reason for this is the good activity of carbon nanotubes in catalyzing the competing hydrogen evolution reaction [35,[[46]](#endnote-46),[[47]](#endnote-47)].

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**Fig. 6.** (A) CV measurements of various carbon supported copper(II) phthalocyanines in CO2-saturated (marked in continuous lines) and N2-saturated (marked in dotted lines) 0.5 M KCl solution. (B) Chronoamperometry measurements of the materials over 1 h under an applied potential of -1.05 V vs RHE. (C) Corresponding product analysis results from chronoamperometry runs. (D) EIS spectra for the materials under study are shown by their Nyquist plots, where CPE stands for constant phase element.

**Table 1.** Faradaic efficiency (FE) of products (in percentages) from chronoamperometry measurements for various carbon supported CuPc. The is obtained from summation of , , , and .

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Electrocatalyst |  |  |  |  |  |  |  |
| Graphene oxide-CuPc | 0.0 | 0.0 | 0.0 | 77.4 | 0.0 | 0.0 | 0.0 |
| Activated carbon-CuPc | 0.0 | 0.0 | 12.8 | 84.3 | 0.0 | 0.0 | 12.8 |
| Carbon nanotube-CuPc | 4.5 | 7.8 | 43.9 | 31.3 | 10.1 | 0.0 | 66.3 |
| Carbon black-CuPc | 5.5 | 5.6 | 45.2 | 20.3 | 10.4 | 15.1 | 81.8 |

To further understand these differences in electrocatalysts performance, electrochemical impedance spectroscopy (EIS) (Fig. 6D) was conducted at the applied potential used for chronoamperometry measurements to compare their charge transfer resistance (RCT), following previous work [46]. The results suggested that carbon nanotube-CuPc had the lowest RCT (20.2 Ω) followed by carbon black-CuPc (22.9 Ω), then activated carbon-CuPc (192.6 Ω) and graphene oxide-CuPc (250.2 Ω). This trend is similar to that observed in the CV and chronoamperometry results. The overall higher performances seen for the carbon nanotube-CuPc and the carbon black-CuPc were possibly due to their lower charge transfer resistances relative to the activated carbon-CuPc and the graphene oxide-CuPc. This could be related to the presence of conductive graphitic structure observed in the carbon nanotube and the carbon black as seen from the XRD results (Fig. S3). Another possibility was due to differences in their electrochemical surface area (ECSA). This was investigated by measuring their capacitance using CV at potentials where Faradaic process was absent [[[48]](#endnote-48)]. Results (shown in SI, Fig. S4) presented the carbon nanotube-CuPc having superior ECSA compared to the other materials, likely contributed by its fine size and tube-like morphology. It is well-known that decreasing the size of materials increases its surface area to volume ratio [[[49]](#endnote-49)-[[50]](#endnote-50)[[51]](#endnote-51)[[52]](#endnote-52)]. The carbon nanotube-CuPc was found to be smaller in size than the other materials, as presented in Fig. 4. This could result in its higher ECSA. Moreover, the tube-like structures of carbon nanotubes have been reported to give higher surface area relative to film and rod-like structures [[[53]](#endnote-53)]. The high ECSA and low RCT value makes carbon nanotubes a superior carbon support for hybridization with metals for electrochemical CO2 reduction.

Apart from studying the preferred carbon support for CO2 electroreduction, it was also insightful to understand why ethanol, a valuable C2 product, was produced in the case of carbon black-CuPc but not for carbon nanotube-CuPc. The electrochemical conversion of CO2 to ethanol is a challenging process requiring transfer of 12 electrons and involving several steps [[[54]](#endnote-54),[[55]](#endnote-55)]. There have been reports which provide evidence of ethanol being favorably formed when reduced Cu species are present in the electrocatalyst [48,[[56]](#endnote-56)]. From the XPS results, a reduced Cu(I) peak was observed for carbon black-CuPc but not for carbon nanotube-CuPc. This reduced Cu(I) peak could be due to the presence of C≡C in carbon black (~2000 cm-1) from FTIR results (Fig. S2). The C≡C bond had been reported to be reactive towards copper-catalyzed electroreduction [[[57]](#endnote-57)]. This could be a plausible reason for the generation of ethanol observed with the electrochemical CO2 reduction by carbon black-CuPc.

*2.3. Electrochemical studies between different carbon nanotubes supported CuPc*

To add further insight into the use of carbon nanotubes as carbon supports for electrochemical CO2 reduction, the effect of different CNTs sizes was investigated. Two additional carbon nanotubes hybridized with CuPc were prepared: (1) carbon nanotubes of shorter length (1-10 µm) but larger in diameter (50-300 nm) compared to former; denoted as carbon nanotube (thick and short), and (2) carbon nanotubes derived from plastic wastes which had similar diameter (10-40 nm) while having shorter length (0.1-1 µm) relative to former; referred to as carbon nanotube (waste derived). Their material characterizations and size distribution analysis are presented in the SI (Fig. S5-9, Table S3-4).

Similar electrochemical measurements were performed (Fig. 7). The CV and chronoamperometry results presented carbon nanotube-CuPc yielding higher current whereas carbon nanotube (thick and short)-CuPc and carbon nanotube (waste derived)-CuPc produced similarly low currents (Fig. 7A,B). In terms of generated products, carbon nanotube (thick and short)-CuPc mainly produced H2 () while carbon nanotube-CuPc and carbon nanotube (waste derived)-CuPc formed more CO2 reduced species such as CO, formic acid, methane and ethylene (Fig. 7C). This imply that among different sizes of carbon nanotubes, long and thin CNTs are preferred carbon supports for electrochemical CO2 reduction over thicker and shorter ones. This finding is similar to a previous work that reported highly curved (i.e. thin diameter) cobalt porphyrin nanotubes had a tendency to produce CH4 while nanotubes of larger diameter favored the formation of CO from CO2 reduction reaction due to different binding energies of reaction intermediates [[[58]](#endnote-58)].

Additionally, our results also demonstrated the novel use of modified waste-derived carbon nanotubes for electrochemical CO2 reduction. Interestingly, the FE results for various carbon products from carbon nanotube (waste derived)-CuPc are similar to those observed for carbon nanotube-CuPc (Table 2). Also, both materials show comparable overall FE conversions to carbon products, i.e. FEC products = 70.4 % for carbon nanotube (waste derived)-CuPc and FEC products = 66.3 % for carbon nanotube-CuPc.

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**Fig. 7.** (A) CV measurements of various carbon nanotube supported copper(II) phthalocyanines in CO2-saturated (marked in continuous lines) and N2-saturated (marked in dotted lines) 0.5 M KCl solution. (B) Chronoamperometry measurements of the materials over 1 h under an applied potential of -1.05 V vs RHE. (C) Corresponding product analysis results from chronoamperometry runs. (D) EIS spectra for the materials under study are shown by their Nyquist plots, where CPE stands for constant phase element.

**Table 2.** Faradaic efficiency (FE) of products (in percentages) from chronoamperometry measurements for various carbon nanotubes supported CuPc. The is obtained from summation of , , , and .

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Electrocatalyst |  |  |  |  |  |  |  |
| Carbon nanotube-CuPc | 4.5 | 7.8 | 43.9 | 31.3 | 10.1 | 0.0 | 66.3 |
| Carbon nanotube (thick and short)-CuPc | 0.0 | 0.0 | 7.4 | 98.8 | 0.0 | 0.0 | 7.4 |
| Carbon nanotube (waste derived)-CuPc | 10.7 | 7.6 | 37.4 | 42.9 | 14.7 | 0.0 | 70.4 |

EIS results (Fig. 7D) revealed that carbon nanotube-CuPc had the lowest RCT value (20.2 Ω) in comparison with carbon nanotube (waste derived)-CuPc (76.7 Ω) and carbon nanotube (thick and short)-CuPc (204.6 Ω). The ECSA measurements also showed a similar trend where carbon nanotube-CuPc has the highest ECSA followed by carbon nanotube (waste derived)-CuPc and then carbon nanotube (thick and short)-CuPc (see SI, Fig. S10). This is likely due to the differences in their size in terms of diameter and length (carbon nanotube-CuPc are thin and long whereas carbon nanotube (thick and short)-CuPc are thicker and shorter while carbon nanotube (waste derived)-CuPc are thin yet short). These results suggest that the better performance observed for carbon nanotube-CuPc arises from its lower charge transfer resistance and larger ECSA.

**3. Conclusion**

In summary, this work compares the use of four different carbon materials, namely graphene oxide, activated carbon, carbon nanotubes and carbon black, which can be used as supports for copper(II) phthalocyanine for electrochemical CO2 reduction. Our results highlighted that carbon nanotubes and carbon black are more efficient carbon supports for CO2 electrocatalyst preparation, owing to their high electrical conductivity. A range of C1 and C2 products were detected (including CO, formic acid, methane, ethylene and ethanol) with carbon black-CuPc showing higher C product conversion compared to carbon nanotube-CuPc. This study was extended to explore the preferred size dimensions of carbon nanotubes as carbon supports. Thin and long nanotubes (in the range of 10-30 nm diameter size and 10-30 µm length) were found to be more electrocatalytic for CO2 electroreduction compared to shorter and thicker ones due to lower charge transfer resistance and larger electrochemical surface area. Additionally, the novel use of plastic waste-derived carbon nanotubes with thin diameter was demonstrated as carbon supports and yielded comparable FE conversion to C products similar to using commercial grade CNTs.

**4. Materials and Method**

Chemicals and materials: Multi-walled carbon nanotubes (MWCNTs) (diameter: 10-20 nm, length: 10-30 µm; diameter: 100-170 nm, length: 5-9 µm), activated charcoal (granular, untreated, grinded and sieved to < 100 µm), copper(II) phthalocyanine (sublimed grade), N,N-dimethyl formamide (DMF), ethanol, 70 % nitric acid, potassium hydroxide pellets, dimethyl sulfoxide (DMSO), deuterium oxide, potassium permanganate (KMnO4), concentrated sulfuric acid (H2SO4), sodium nitrate (NaNO3), 30% hydrogen peroxide (H2O2) were obtained from Sigma Aldrich. Nafion (D-520 dispersion) and Toray carbon paper (TGP-H-60) were purchased from Alfa Aesar. Carbon black Vulcan XC72 was received from Cabot.

Synthesis of waste-derived carbon nanotubes: The synthesis method was similar to that reported previously [[[59]](#endnote-59)]. In brief, flexible plastic packaging waste was used as a feedstock and contained 53.0 wt.% polyethylene, 28.2 wt.% propylene, 11.8 wt.% polyethylene terephthalate, 1.3 wt.% polyamide, 1.1 wt.% printing inks, 3.7 wt.% aluminium and 1.0 wt.% adhesive inks. The synthesis of MWCNTs was carried out in a three-step process. Plastic waste was pyrolyzed at 500 oC in a batch pyrolysis reactor causing the decomposition of polymers. The produced volatile species were further treated in the second reactor at 400 oC over iron supported ZSM-5 catalyst in order to decompose oxygenated hydrocarbons. These oxygenated hydrocarbons are typically produced due to the decomposition of polyethylene terephthalate contained in the postconsumer plastic waste. After catalytic treatment, volatile products were cooled down to 40-50 oC for oil condensation. Non-condensable pyrolysis gas exiting oil condenser was used for the synthesis of MWCNTs via chemical vapor deposition over NiO supported on CaCO3 catalyst at 700 oC. The synthesized MWCNTs were washed with hydrochloric acid followed by deionized water until pH 5 and dried at 105 oC.

Synthesis of graphene　oxide: The synthesis method of graphene oxide was similar to that reported previously [[[60]](#endnote-60)]. In brief, the sodium nitrate (0.5 g) was dissolved in H2SO4 concentrated (23.3 ml) in an ice bath. After that, 2.5 g KMnO4 and 0.5 g pure graphite powder were added gradually. The temperature was kept below 20 oC and stirred continuously for 2 hours. The temperature was then raised and stirred at 40 oC using hot plate with magnetic stirrer for 14 hours. Subsequently, 21 mL of distilled water was poured into the solution, stirred for another 30 min, before adding 3.3 mL 35% hydrogen peroxide (H2O2). The addition of H2O2 turned the solution yellow. For purification, 133 mL of distilled water and 5% HCl aqueous solution were added. The mixture was washed by rinsing and centrifugation with deionized water several times to neutral pH. The solution was then filtered and dried at 80 oC to obtain graphite oxide. The dried graphite oxide was grinded until it became powdered form. This powder was then dispersed in deionized water and exfoliation was done by sonication for 1 hour.

Material characterization: The FESEM-EDS images were taken using JEOL, JSM-7600F at a working distance of 10 mm and 10 kV accelerating voltage while TEM images were captured using JEOL, JEM-1400Plus. The FTIR measurements were made using Shimadzu IR Prestige 21. XRD analysis was obtained with a Cu-Kα radiation source in the 2θ range between 10 to 80 o, step size of 0.035 o and 0.3 s per step (PANalytical XPert Pro). The XPS data was collected using Kratos Axis Supra spectrometer and calibrated against adventitious carbon at 284.5 eV, identified via high resolution C 1s scan. Copper content was determined using acid microwave digestion of 10 mg samples in 10 mL 70 % nitric acid at 175 oC for 20 min, followed by filtration and dilution of samples before analyzing them with the ICP-OES (Perkin Elmer Optima 8000).

Catalyst preparation: The preparation of the hybrid materials was similar to that reported previously [20]. In brief, the carbon supports (30 mg) were dispersed in 30 mL DMF and sonicated for 1 h. Following that, 30 mg of copper(II) phthalocyanine dissolved in DMF was introduced and the solution was sonicated for another 30 min. Subsequently, the suspensions were additionally stirred for 24 h at room temperature. After that, they were centrifuged and the solid washed with DMF thrice and later with ethanol twice, before finally freeze drying the precipitate. In the case of activated carbon, it was first grinded using a mortar and pestle and then sieved through a 100 µm strainer.

Working electrode preparation: 2 mg of the prepared catalyst material was weighed and sonicated with 870 µL ethanol for 1 h to obtain a well dispersed suspension. Thereafter, 130 µL Nafion was added as a binder. About 10 µL of the liquid was then dropcasted on carbon paper and hand-painted to cover an area of 1 cm by 1 cm. The catalyst was then dried under a lamp at room temperature.

Electrochemical study: Electrochemical measurements were done using Gamry Interface 1000 potentiostat. The cyclic votammetry (CV) was conducted in CO2-saturated or N2-saturated 0.5 M KCl solution at a scan rate of 50 mV/s in a three-electrode setup with platinum foil as a counter electrode, catalyst deposited on carbon paper as the working electrode and Ag/AgCl (saturated KCl) as the reference electrode. Pure CO2 (99.995%, Leedon NOX) and high purity nitrogen (99.9995%, Leeden NOX) were used for the gas saturation. The EIS was performed under 5 mV AC amplitude at a frequency range between 100 kHz and 0.1 Hz, with applied DC voltage of -1.6V versus Ag/AgCl (saturated KCl) reference electrode in CO2-saturated 0.5 M KCl solution. The fitting was done using a modified Randles circuit [45]. The electrochemical surface area (ECSA) measurement was conducted by running CVs between 50 mV to -50 mV in 0.1 M KOH solution at different scan rates [48]. For chronoamperometery measurements, a H-cell was used with 10 mL 0.5 M KCl solution in the cathode compartment and 7 mL 3 M KHCO3 in the anode compartment. The two compartments were separated by an anion exchange membrane (Selemion). Prior to the run, 20 sccm CO2 was bubbled into the catholyte for at least 30 min. Subsequently, the CO2 flowrate was changed to 11 sccm for the 1 h chronoamperometry run. The distance between the working electrode and the Ag/AgCl reference electrode was adjusted to be less than 1 cm to reduce the effect of iR drop to negligible. The applied potentials were rescaled to the reversible hydrogen electrode (RHE) using the following equation: E (vs RHE) = E (vs Ag/AgCl) + 0.197 V + (0.0591 x pH) [[[61]](#endnote-61),[[62]](#endnote-62),[[63]](#endnote-63)].

Product analysis: Gas samples from the cathode compartment were collected in gas bags every 20 min and analyzed using gas chromatography equipped with thermal conductivity detector and flame ionization detector (Agilent, GC-TCD-FID 7890B). After the 1h chronoamperometry measurement, the liquid products in catholyte was analyzed using 1H NMR (JEOL, ECA400). The 100 µL of the liquid sample was mixed with 400 µL D2O and 100 µL 1.25 mM DMSO as internal standard [[[64]](#endnote-64)]. The concentrations of formic acid and ethanol were determined using calibration graphs of the pure liquids. Their calibration plots are available in the supporting information (Fig. S11).

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgement**

The authors would like to thank NEWRI (Nanyang Technological University) and Singapore’s Economic Development Board (EDB) for their financial support in this research. In addition, the Academy of Finland (project number 295019) is acknowledged for the financial support.

**Notes and references**

The supporting information (SI) contains additional material characterization, ECSA results, metal content of materials under study, pH values of CO2- and N2-saturated 0.5 M KCl solution as well as calibration plot for NMR detection of formic acid and ethanol.

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