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# A Nitrogen-Doped Carbon Catalyst for Electrochemical CO<sub>2</sub> Conversion to CO with High Selectivity and Current Density

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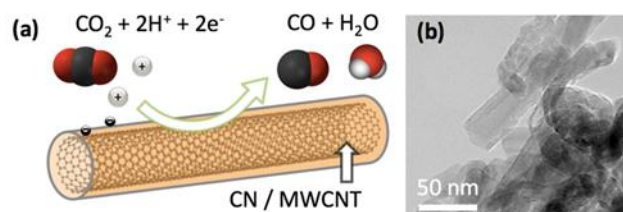
**Abstract:** We report characterization of a non-precious, metal-free catalyst for the electrochemical reduction of CO<sub>2</sub> to CO; namely, a pyrolyzed carbon nitride and multiwall carbon nanotube composite. This catalyst exhibits a high selectivity for production of CO over H<sub>2</sub> (~98% CO and ~2% H<sub>2</sub>), as well as high activity in an electrochemical flow cell. The CO partial current density at intermediate cathode potentials ( $V = -1.46$  V vs. Ag/AgCl) is up to 3.5x higher than state-of-the-art silver nanoparticle-based catalysts, and the maximum current density is 90 mA/cm<sup>2</sup>. The mass activity and energy efficiency (up to 48%) were also higher than the Ag nanoparticle reference. Moving away from precious metal catalysts without sacrificing activity or selectivity may significantly enhance the prospects of electrochemical CO<sub>2</sub> reduction as an approach to reduce atmospheric CO<sub>2</sub> emissions or as a method for load-leveling in relation to the use of intermittent renewable energy sources.

## Introduction

Rising carbon dioxide levels as a result of human activity have been linked to climate change, leading to e.g. erratic weather patterns and rising ocean temperatures.<sup>[1]</sup> Multiple approaches should be implemented to curb this increase in CO<sub>2</sub> concentration, including carbon sequestration, electrification of the transportation sector, and switching from using fossil fuels to renewable energy.<sup>[2,3]</sup> A major challenge in the implementation of wind and solar -derived renewable energy is intermittency, i.e. the mismatch between supply and demand. Bridging this gap will require the development of scalable and broadly deployable mass electricity conversion and storage technologies. One interesting method to reduce CO<sub>2</sub> emissions as well as providing a means of mass energy storage, is the electrochemical reduction of CO<sub>2</sub> into useful chemicals which can then be stored or transported at scale, and used on demand.<sup>[4–6]</sup> However, catalysts for the electrochemical reduction of CO<sub>2</sub> into products such as CO, formic acid, methanol, and small hydrocarbons currently do not exhibit sufficient activity or selectivity for such

applications. Metals such as silver (Ag), and gold (Au), exhibit the best performance for conversion of CO<sub>2</sub> to CO to date.<sup>[4,7–9]</sup> However, high cost, sensitivity to poisoning, difficulty of reclamation, and insufficient activity hampers their utility and wide-scale adoption.

In the parallel field of fuel cells, high cost, limited durability, and susceptibility of Pt-group electrocatalysts to poisoning have spurred intensive research into alternatives. This includes reducing Pt-loading by using alloys; and the use of non-platinum group metal (non-PGM) catalysts for the oxygen reduction reaction (ORR). Non-PGM electrocatalysts are often variations on nitrogen-coordinated iron or cobalt in a carbon matrix (*i.e.*, Fe/N/C, Co/N/C), or simply metal-free nitrogen-doped carbon.<sup>[10,11]</sup> Nitrogen-doped carbon nanotube powders,<sup>[12]</sup> nanotube arrays,<sup>[13]</sup> graphene,<sup>[14,15]</sup> nanocages,<sup>[16]</sup> and carbon nitrides,<sup>[17–22]</sup> have been studied in recent years for reactions including: (i) the ORR,<sup>[17–22]</sup> (ii) photocatalytic water splitting,<sup>[23,24]</sup> and (iii) photocatalytic CO<sub>2</sub> reduction. In (iii), the primary products include CO, methanol and ethanol, but at low quantum yield.<sup>[25,26]</sup> We have demonstrated that carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) exhibits ORR activity, especially when synthesized on a conductive support with large surface area.<sup>[19–22]</sup> High temperature treatment played a critical role in the catalytic activity, with optimal activity achieved after pyrolysis at 1000°C.<sup>[20,21]</sup> Such catalysts contain only carbon and nitrogen with trace amounts of dopants / impurities, and are synthesized by simple and scalable methods. Additionally, we have developed organometallic silver heterogeneous catalysts for the CO<sub>2</sub> reduction reaction involving nitrogen-containing organic ligands.<sup>[27]</sup>



**Figure 1.** (a) Schematic representation of the electrochemical CO<sub>2</sub> reduction reaction on a carbon nitride-coated multiwall carbon nanotube. (b) TEM image of the synthesized CN/MWCNT catalyst powder.

The above work led us to the conclusion that such non-PGM nitrogen-doped carbon catalysts should be more thoroughly explored for the electrochemical CO<sub>2</sub> reduction reaction. Relatively few examples of the use of this class of catalyst for

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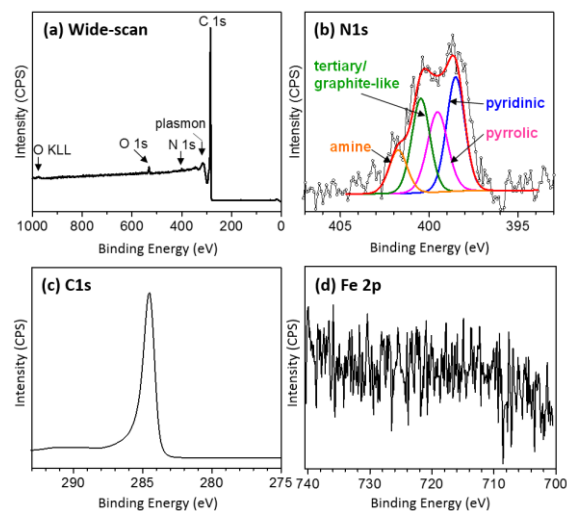
CO<sub>2</sub> reduction exist. Kumar *et al.* reported a nitrogen-doped carbon fiber catalyst fabricated by pyrolysis of electrospun mats of polyacrylonitrile (PAN). The micron-scale fibers exhibited some activity for CO<sub>2</sub> reduction to CO, with a current density of up to 5 mA/cm<sup>2</sup> in a standard 3-electrode cell.<sup>[28]</sup> Zhang *et al.* achieved CO<sub>2</sub> reduction on nitrogen-doped carbon nanotubes in aqueous bicarbonate solutions, with a faradaic efficiency of 59%.<sup>[29]</sup> Recently, Wu *et al.* achieved a selectivity of 80% and a partial current density for CO formation of 2.25 mA/cm<sup>2</sup>.<sup>[30]</sup> Here we explore non-precious, metal-free, nitrogen-doped carbon catalysts for the electrochemical reduction of CO<sub>2</sub> to CO. This can then be converted into liquid fuels by using e.g. the Fischer-Tropsch process. Specifically, the materials are comprised of carbon nitride (CN) supported on multiwall carbon nanotubes (MWCNTs), subjected to pyrolysis at 1000°C to form CN/MWCNT nanocomposites (Figure 1a).

## Results and Discussion

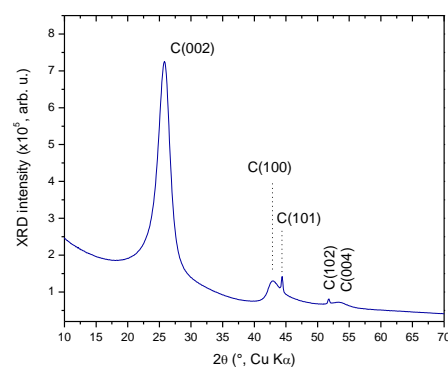
Characterization of the CN/MWCNT powder by transmission electron microscopy (TEM) reveals short, defective, and kinked MWCNTs, structural characteristics introduced during the milling step (Figure 1b). The surface area was measured to be 250.2 m<sup>2</sup>/g by nitrogen adsorption. CHN elemental analysis reveals a nitrogen content of 0.39 at%. This low nitrogen content reflects the fact that the pyrolysed carbon nitride exists as a thin layer on the surface of the pure carbon MWCNT. The nitrogen content of this thin layer is expected to be higher, but the composition of such a thin layer is difficult to determine using conventional characterization techniques. Peaks in the X-ray photoelectron spectroscopy (XPS) survey spectra (Figure 2a) are attributed to carbon (97.68 at.%), nitrogen (0.12 at.%) and oxygen (2.20 at.%). Deconvolution of the N1s peak reveals the probable presence of pyridinic (~398.5 eV, 33.4%), pyrrolic (399.5 eV, 26.3%), tertiary/graphite-like (~400.5 eV, 27.6%), and amine (401.7 eV, 12.7%) nitrogen environments (Figure 2b), arising from pyrolysis of the initial carbon nitride coating. Metal impurities (especially Fe) are absent within the detection limits of the machine (Figure 2d), however, trace amounts of the metal may be present as contamination from the stainless steel reaction vessel. The XRD spectrum (Figure 3) is as typically observed for MWCNTs, with sharp peaks corresponding to the 002, 110, and 101 lattice planes of carbon. The nitrogen-doped carbon coating is expected to have broad, low intensity peaks at around 25° and 44° reflecting low crystallinity.<sup>[15]</sup> However, these are masked by the intense MWCNT signal, reflecting the relatively thin nature of the nitrogen-doped carbon coating.

The activity of the CN/MWCNT catalyst for electroreduction of CO<sub>2</sub> was determined and compared it with a state-of-the-art Ag nanoparticle catalyst. Cyclic voltammetry (CV) was performed in a 3-electrode cell. CN/MWCNT exhibits around five times higher activity for CO<sub>2</sub> conversion compared to the Ag nanoparticles, although the Ag catalyst displays an earlier onset potential (Figure 4). This result suggests promise for application of the

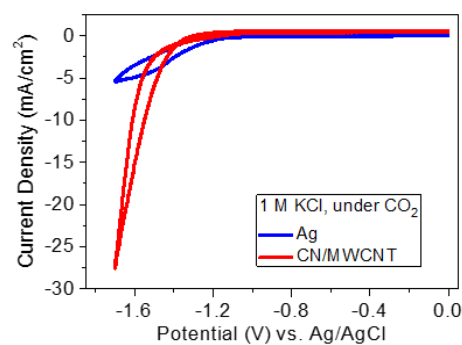
CN/MWCNT in CO<sub>2</sub> electrolysis, especially at high current densities.



**Figure 2.** (a) Full XPS survey spectrum of the CN/MWCNT catalyst, and (b) high resolution spectrum of the N1s region. XPS spectrum Fe 2p region of the CN/MWCNT sample.



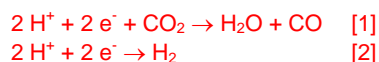
**Figure 3.** XRD spectrum of the CN/MWCNT catalyst.



**Figure 4.** Cyclic voltammetry measuring the CO<sub>2</sub> reduction activity of the CN/MWCNT and Ag catalysts in a standard 3-electrode electrochemical cell (1M KCl, 25 mV/s).

Subsequently, the CO<sub>2</sub> reduction activity was tested using a CO<sub>2</sub> electrolysis cell.<sup>[7]</sup> The cathode electrocatalyst was sprayed onto a carbon paper gas diffusion electrode (GDE) and assembled into the cell. Analysis via X-ray micro-computed tomography (MicroCT) reveals a uniform and crack free electrocatalyst layer (Figure 4a) supported on the highly porous GDE. Cross-sectional observation using scanning electron microscopy (SEM) confirms that the CN/MWCNT catalyst layer uniformly coats the GDE with a thickness of around 15 μm (Figure 5b). Higher magnification SEM images of the CN/MWCNT electrocatalyst layer reveal agglomerates of varying sizes at the micron-scale (Figure 5c). This microstructure may improve the accessible surface area and enhance mass diffusion through the electrocatalyst layer.

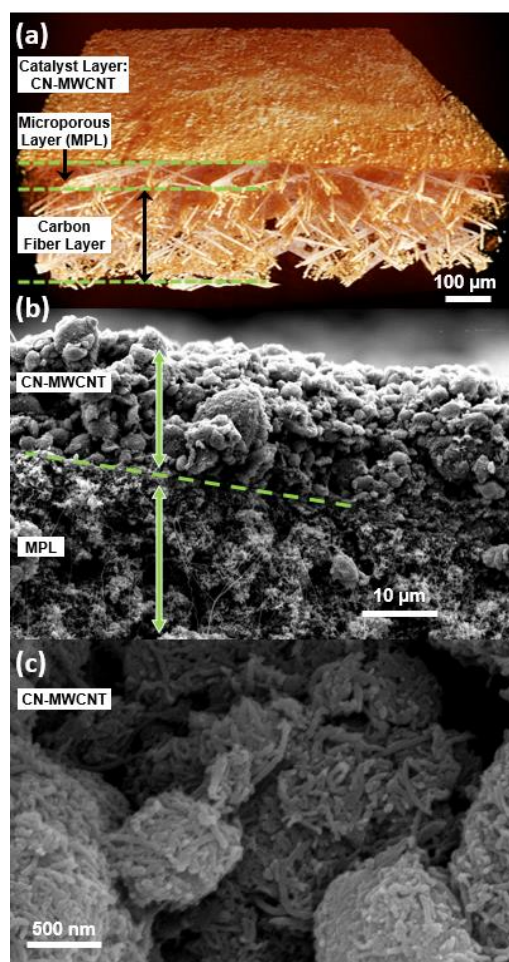
Figure 6 shows the performance of the microfluidic CO<sub>2</sub> electrolysis cell operated with the CN/MWCNT catalyst, and compared with Ag nanoparticles. The anode reaction is Cl<sub>2</sub> evolution, given that the electrolyte used is 1M KCl. **Only H<sub>2</sub> and CO were detected as products at the cathode, and the following are likely reaction mechanisms:**



The CN/MWCNT cathode catalyst displays significantly higher CO partial current density than the Ag catalyst at cathode potentials of -1.2 ~ -1.6 V vs. Ag/AgCl, revealing that the CN/MWCNT catalyst is highly active for the conversion of CO<sub>2</sub> to CO (Figure 6a). The cell produces a partial CO current density of up to 90 mA/cm<sup>2</sup> at a cathode potential of -1.62 V vs. Ag/AgCl, when operated with the CN/MWCNT cathode catalyst. **These values are much higher than those previously reported in the literature for other nitrogen-doped carbon systems.<sup>[28–30]</sup> The performance was stable at least over a period of several hours.** Furthermore, the CO partial current density for CN/MWCNT is up to 3.5 times higher than the state-of-the-art Ag nanoparticle-based catalyst at intermediate cathode potential (V=-1.46 V vs. Ag/AgCl). The mass activity (i.e. normalized to catalyst loading) gives a clearer comparison between the two catalysts. In this case, at -1.46 V vs. Ag/AgCl, the mass activity of CN/MWCNT is 29.2 A/g, compared with 26.7 A/g for the Ag nanoparticles. This indicates that the non-precious catalysts actually have comparable mass activity to the current state-of-the-art at this intermediate cathode potential.

The CN/MWCNT catalyst also catalyzes hydrogen formation to a small extent, whereas the Ag cathode produces nearly no hydrogen within the detection limit of the gas chromatograph. Figure 5b indicates that CN/MWCNT exhibits excellent selectivity for CO, over H<sub>2</sub>, i.e., ~98% CO and ~2% H<sub>2</sub>. Again, this is much higher than values previously reported in the literature.<sup>[28–30]</sup> The overall energetic efficiency is the fraction of energy supplied to the reactor that is successfully transferred to chemical bonds in the desired product. Here, values of 48% and 44% are obtained for the CN/MWCNT cathode catalyst at -1.46 V vs. Ag/AgCl (-2.75 V cell potential) and -1.62 V vs. Ag/AgCl (-

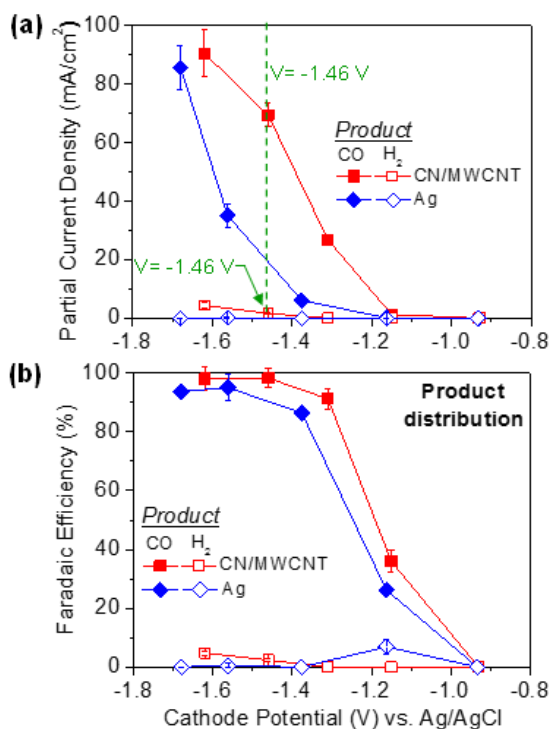
3.0 V cell potential), respectively. In comparison, the Ag catalyst exhibits an energetic efficiency of just 42% at a cathode potential of -1.68 V vs. Ag/AgCl (-3.0 V cell potential). The slightly higher energy efficiency observed for CN/MWCNT can be attributed to the better selectivity for CO over H<sub>2</sub> (Figure 6b). In short, the CN/MWCNT catalyst exhibits high activity, selectivity, and efficiency for the electrochemical reduction of CO<sub>2</sub> to CO, with better performance than other catalysts reported to date, including state-of-the-art silver nanoparticle catalysts.<sup>[7]</sup>



**Figure 5.** (a) Reconstructed 3D view of the electrode obtained from MicroCT data. (b) SEM cross-sectional image of the CN/MWCNT catalyst layer on the microporous layer of the gas diffusion electrode. (c) SEM images of the CN/MWCNT electrocatalyst layer (loading 2.39 mg/cm<sup>2</sup>).

The origin of electrochemical CO<sub>2</sub> reduction activity in nitrogen-doped carbons was recently investigated by comprehensive density functional theory calculations.<sup>[30,31]</sup> These revealed that nitrogen incorporation modifies the electronic properties of carbon, resulting in a reduced energy barrier for the formation of a COOH intermediate (the rate-limiting step). Nitrogen doping also results in strong adsorption of the COOH intermediate, and weak adsorption of the CO or HCOOH products. However, in

these studies, the highest catalytic activity was exhibited by pyrrolic nitrogen sites, leading exclusively to HCOOH as the product.<sup>[30]</sup> This is in contrast to the experimental results reported here in which a mixture of different nitrogen types was detected, and no formic acid was detected in the product stream. This suggests that more work needs to be done to reconcile experiment and theory. This will be the subject of future work.



**Figure 6.** Electrochemical characterization of the CN/MWCNT and Ag catalysts: (a) Partial current densities vs. cathode potential for CO and H<sub>2</sub>; (b) Faradaic efficiency vs. cathode potential for CO and H<sub>2</sub>. The error bars represent the standard deviation of the average of three experiments each with freshly prepared working electrodes (N=3). Cathode catalyst: 2.39 mg/cm<sup>2</sup> CN/MWCNT or 0.75 mg/cm<sup>2</sup> unsupported Ag nanoparticles. Anode catalyst: 4.25 mg/cm<sup>2</sup> unsupported Pt black. Reactant streams: 7 sccm CO<sub>2</sub>; 1.0 M KCl electrolyte flowing at 0.5 mL/min. Data was collected at room temperature and at ambient pressure.

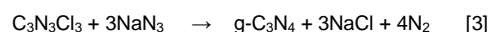
## Conclusions

In summary, we report a non-precious nitrogen-doped carbon catalyst for the electrochemical reduction of CO<sub>2</sub> to CO in an electrochemical flow cell. This exhibits low onset potential, and high current density, selectivity, as well as energetic efficiency, **outperforming results obtained in the existing literature for other nitrogen-doped carbon systems.** Despite the early stage of development, this catalyst already outperforms state-of-the-art silver nanoparticle catalysts. Moving away from precious metal catalysts without sacrificing activity or selectivity offers hope for electrochemical CO<sub>2</sub> reduction to become an economically viable process, by largely reducing the capital cost. Further experimental and computational efforts are required to better

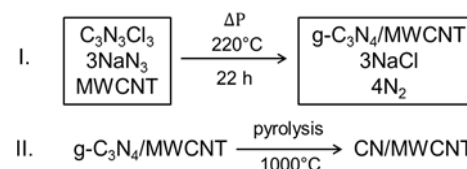
understand the catalytic mechanism, and to further optimize the cell performance.

## Experimental Section

**Preparation of the CN/MWCNT catalyst (Scheme 1):** Cyanuric chloride (1,3,5-trichlorotriazine, C<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub>), sodium azide (NaN<sub>3</sub>), benzene, and multiwall carbon nanotubes (*cheaptubes.com*) were added to a magnetically stirred, stainless-steel high pressure reactor. All materials were used as-received without further purification. The reactor was heated to 220°C for 22 hours, and the cyanuric chloride and sodium azide reacted to yield MWCNTs coated with graphitic carbon nitride,<sup>[32–34]</sup> according to the scheme:<sup>[21]</sup>



The products were removed from the reactor, washed with benzene and Millipore water, and then heated overnight at 80°C under vacuum. Subsequently the material was milled in silicon carbide pots, and then subject to pyrolysis at 1000°C in flowing N<sub>2</sub>. **Surface area was performed by BET nitrogen adsorption analysis (Belsorp mini II-VS, Bel Japan, Inc.).**



**Scheme 1.** Synthesis of the CN/MWCNT catalyst

**Preparation of the Ag nanoparticle catalyst:** Ag nanoparticles were purchased from Sigma Aldrich (nominal size, <100 nm). The actual average particle size was measured as 70 nm by dynamic light scattering, and confirmed by TEM.<sup>[35]</sup>

**Transmission electron microscopy (TEM):** TEM was used to determine the morphology of the CN/MWCNT catalyst (JEOL, JEM2010), operated at 200 kV. The CN/MWCNT powder was suspended in isopropyl alcohol (Sigma-Aldrich) and sonicated for 30 minutes to ensure good catalyst dispersion. TEM grids were prepared by dropping the dilute suspension onto copper grids, which were then dried overnight.

**Elemental analysis:** A CHN elemental analyzer (Yanaco, CHN corder MT-6) was used to determine the nitrogen content of the CN/MWCNT sample. X-ray photoelectron spectroscopy (XPS) was carried out to characterize the chemical composition and nitrogen types in the carbon matrix of CN/MWCNT. XPS spectra were collected using a Kratos Axis ULTRA X-ray photoelectron spectrometer with monochromatic Al K-alpha excitation, 120 W (120 kV, 10 mA). Data were collected using a hybrid lens setting with a slot aperture of 300 x 700 mm<sup>2</sup> analytical area. Charge neutralizer settings of 2.1 A filament current, 2.1 V charge balance and 2V filament bias were used. Survey spectra were collected at a pass energy of 160 eV and high resolution spectra were collected using a pass energy of 40 eV. The data were fitted to Gaussian-Lorentzian curves. The binding energy was referenced to the graphitic C1s line at 284.5 eV.

**Preparation of Electrodes:** Previously we reported the preparation of GDEs for use in a CO<sub>2</sub> electrolysis cell.<sup>[7]</sup> Sigracet 35 BC gas diffusion layers (GDLs, Ion Power) were used, which consist of 5 wt% poly-

tetrafluoroethylene (PTFE)-treated carbon paper that has a teflonized microporous layer on one side. Here the cathodes were air-brushed whereas the anode was hand-painted using previously described methods.<sup>[7]</sup> For the Ag cathodes, catalyst inks were prepared by mixing 2.42 mg Ag, 1.85  $\mu\text{L}$  Nafion solution, 200  $\mu\text{L}$  Millipore water, and 200  $\mu\text{L}$  isopropyl alcohol. For the CN/MWCNT cathodes, catalyst inks were prepared by mixing 6.95 mg CN/MWCNT catalyst, 5.33  $\mu\text{L}$  Nafion solution, 200  $\mu\text{L}$  Millipore water, and 200  $\mu\text{L}$  isopropyl alcohol. For the hand-painted anodes, catalyst inks were prepared by mixing 10 mg Pt black (Alfa Aesar), 6.9  $\mu\text{L}$  Nafion solution, 400  $\mu\text{L}$  of Millipore water, and 400  $\mu\text{L}$  isopropyl alcohol. The catalyst loading of the GDEs was determined by weighing the GDE before and after deposition. The Ag cathodes were coated with 0.75 mg(Ag)/cm<sup>2</sup> and the CN/MWCNT cathodes were covered with 2.39 mg (CN/MWCNT)/cm<sup>2</sup>. The same anode was used for all measurements, with a catalyst loading of 4.25 mg/cm<sup>2</sup> Pt black. All inks were sonicated for 20 minutes to ensure uniform mixing and were either hand-painted using a paintbrush or air-brushed using an automated air-brushing deposition setup onto the teflonized carbon side of the GDL to create a GDE covered with catalyst over a geometric area of 2 cm<sup>2</sup>.

**Scanning electron microscopy (SEM):** The morphology of the CN/MWCNT catalyst particles within the catalyst layer of the GDE was characterized using SEM (Philips XL30 ESEM-FEG). For cross-sectional images the GDE was broken via liquid nitrogen cracking using a razor blade and the images were acquired using an acceleration voltage of 7.5 kV, a spot size of 3.0 nm, and a working distance of 10.7 mm. Top-down images were acquired using an acceleration voltage of 7.5 kV, a spot size of 2.0 mm, and a working distance of 7.5 mm.

**Micro-computed X-ray tomography (MicroCT):** We used the same acquisition and reconstruction procedures as reported in our prior work.<sup>[36]</sup> In short, the whole GDE was clamped in a rotating sample holder and a corner was exposed to the X-ray beam field. During MicroCT imaging (Micro-XCT 400, Xradia), the sample was scanned using an X-ray source at 40 kV and 200  $\mu\text{A}$ , and 745 projections were collected as the sample was rotated stepwise over 180° with a 10 second exposure time for each projection. The projection images were then processed to reconstruct 2D radiographic cross-sectional image stacks and 3D tomographic virtual models of the GDE. The initial reconstruction of MicroCT data was conducted using the *TXM Reconstructor* reconstruction software (Xradia), which accompanies the MicroCT hardware. The distances of the sample to the X-ray source (76 mm) and the X-ray detector (28 mm) resulted in a voxel (volume pixel) size of 1  $\mu\text{m}^3$ . The field of view (FOV) was approximately 1000  $\mu\text{m} \times 1000 \mu\text{m}$ .

**Electrochemical flow cell measurements:** Two catalyst-coated GDEs, an anode and a cathode, were placed on opposite sides of a 0.15-cm thick poly(methyl methacrylate) (PMMA) sheet with a 0.5 cm wide by 2.0 cm long window (1 cm<sup>2</sup>) such that the catalyst layers faced the flowing liquid electrolyte. The geometric surface area used to calculate current density was 1 cm<sup>2</sup>. This three-layer assembly was clamped between two aluminum current collectors with access windows. On the cathode side an aluminum gas flow chamber supplied CO<sub>2</sub> while the anode was open to the atmosphere so formed O<sub>2</sub> can escape. The assembly was held together with 4 bolts with Teflon washers to maintain electric isolation between electrodes. CO<sub>2</sub> electrolysis experiments were conducted using a potentiostat (Autolab PG30) at room temperature and ambient pressure. CO<sub>2</sub> gas (S.J. Smith, 100%) was fed at a rate of 7 sccm. In all experiments, the electrolyte flow rate was 0.5 mL/min controlled by a syringe pump (Harvard Apparatus PhD 2000). The electrolyte was 1 M potassium chloride (KCl, Sigma-Aldrich, >99.9995% pure) in water. Millipore water was used for all electrolytes. Electrolysis cell polarization curves were obtained by steady-state chronoamperometric

measurements in which gaseous products, as well as unreacted CO<sub>2</sub>, were collected and injected into a gas chromatograph (Trace GC, ThermoFisher Scientific) equipped with a thermal conductivity detector for quantitative determination of product composition. Individual anode and cathode polarization curves were independently measured using an external Ag/AgCl reference electrode which was ionically connected to the electrolyzer.

**Electrochemical data analysis:** The Faradaic efficiency ( $FE_k$ ) of a gaseous product  $k$  was calculated using the following equation:

$$FE_k = \frac{n_k F x_k F_m}{I}$$

Where  $n_k$  is the number of electrons exchanged ( $n_k = 2$  for reduction of CO<sub>2</sub> to CO),  $F$  is Faraday's constant ( $F = 96485 \text{ C/mol}$ ),  $x_k$  is the mole fraction of the gaseous product  $k$  in the gaseous mixture (also equal to the volume fraction if gases are assumed to be ideal),  $F_m$  is the molar flow rate (mol/s), and  $I$  is the total current (A). Specifically, we calculated  $x_k$  and  $F_m$  using the following equations:

$$x_k = \frac{F_{v,CO}}{F_{v,CO} + F_{v,CO_2}} = \frac{F_{v,CO} / F_{v,CO_2}}{1 + F_{v,CO} / F_{v,CO_2}}$$

$$F_m = \frac{PF_v}{RT}$$

Where  $F_{v,CO}$  and  $F_{v,CO_2}$  are the volumetric flow rates (cm<sup>3</sup>/s) of CO and CO<sub>2</sub>, respectively.  $P$  is the atmospheric pressure ( $P = 1 \text{ atm}$ ),  $R$  the gas constant ( $R = 82.06 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ ), and  $T$  the temperature ( $T = 293 \text{ K}$ ). The energetic efficiency ( $EE_k$ ) for the gaseous product  $k$  was calculated using the following equation:

$$EE_k (\%) = \frac{E^o}{V_{cell}} \times FE_k (\%)$$

Where  $E^o$  is the equilibrium cell potential ( $E^o = E^o_{cathode} - E^o_{anode} = -0.10 \text{ V} - 1.23 \text{ V} = -1.33 \text{ V}$  for CO<sub>2</sub> reduction to CO and  $E^o = E^o_{cathode} - E^o_{anode} = 0 \text{ V} - 1.23 \text{ V} = -1.23 \text{ V}$  for H<sub>2</sub> evolution),  $V_{cell}$  is the applied cell potential, and  $FE_k$  is the Faradaic efficiency of the gaseous product  $k$ . The overall cell energetic efficiency is the sum of the energetic efficiencies for CO and H<sub>2</sub>.

## Acknowledgements

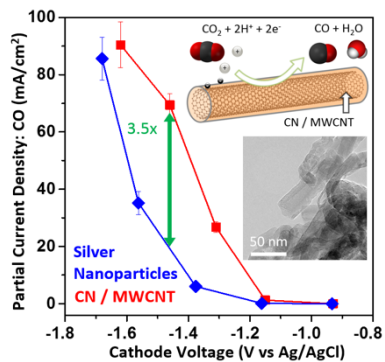
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**Keywords:** CCU • non-precious • catalysis • metal-free • CO<sub>2</sub> conversion

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