Molecular cobalt corrole complex for the heterogeneous electrocatalytic reduction of carbon dioxide

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Electrochemical conversion of CO2 to alcohols is one of the most challenging methods of conversion and storage of electrical energy in the form of high-energy fuels. The challenge lies in the catalyst design to enable its real-life implementation. Herein, we demonstrate the synthesis and characterization of a cobalt(III) triphenylphosphine corrole complex, which contains three polyethylene glycol residues attached at the meso-phenyl groups. Electron-donation and therefore reduction of the cobalt from cobalt(III) to cobalt(I) is accompanied by removal of the axial ligand, thus resulting in a square-planar cobalt(I) complex. The cobalt(I) as an electron-rich supernucleophilic d8-configurated metal centre, where two electrons occupy and fill up the antibonding dz2 orbital. This orbital possesses high affinity towards electrophiles, allowing for such electronically configurated metals reactions with carbon dioxide. Herein, we report the potential dependent heterogeneous electroreduction of CO2 to ethanol or methanol of an immobilized cobalt A3-corrole catalyst system. In moderately acidic aqueous medium (pH = 6.0), the cobalt corrole modified carbon paper electrode exhibits a Faradaic Efficiency (FE%) of 48 % towards ethanol production.

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Minimizing of the CO2 concentration in the atmosphere is one of the most important challenges in our time\(^1,2\). Therefore, the electrochemical reduction of CO2 to value added chemicals is a sustainable strategy to solve the growing energy crisis, which at the same time has the potential to mitigate environmental pollution. In the past years, the electrochemical reduction of CO2 has been studied by several research groups to produce valuable products, for example carbon monoxide, formic acid, methane, ethanol, or methanol\(^3-5\). Particularly the transformation of CO2 in high-density alcohols, especially methanol and ethanol, is a cherished goal for chemists and environmental engineers alike\(^6,7\). Such transformation of CO2 to alcohols coupled with the oxidation of water to oxygen\(^8\) is a promising strategy\(^9\). However, the low reactivity of carbon dioxide in water with its large energy barrier (\(\Delta E = -1366.8 \text{kJ mol}^{-1}\))\(^10\) and the competing hydrogen evolution reaction, impedes such transformation, which makes the development of catalysts for electrocatalytic CO2 reduction to ethanol in aqueous environment a big challenge\(^1,2,10\). The thermodynamic reduction potential for CO2 to methanol and ethanol is 0.03 and 0.09 V (vs. RHE), respectively\(^11\), which is kinetically disfavored. Hence, often CO2 reducing catalysts end up accruing lot of energy to be operational at a higher potential. In this regard the usage of a molecular catalyst with earth abundant elements, (Fe, Mn, Co, Cu, and Ni), especially with a cobalt metal center\(^11,12\) is a viable alternative as it offers a high degree of tunability with product selectivity at a low overpotential. As early as in 1980s chemists have been successful in reducing CO2 to CO via electrochemical methods employing catalysts containing different metals like Co\(^13\), Ni\(^14\), Re\(^15-17\), etc. Recently electrochemical reduction of CO2 to ethanol has been studied in various ways\(18,19\), by tuning the applied potential\(20\), pH\(^21\), and nature of the electrolyte\(^22\) with an aim to control the product selectivity and increase the Faradic efficiency (FE) as well as to understand the underlying mechanistic pathways. Metal surfaces\(23,24\), oxides\(^25\), and alloys\(^26,27\) are the most explored examples which show good FE for CO2 reduction but lack selectivity\(^28,29\) and work at higher overpotentials, involving complex synthetic procedures\(^30,31\). Emergent materials like B and N co-doped nanodiamonds exhibit excellent FE (93\%) and selectivity for conversion to ethanol, but work at higher overpotentials\(^32\). Moreover such heteroatom-doped materials\(^33\) often require a sophisticated synthetic procedure like chemical vapor deposition, making it hard for large scale implementation\(^34\). We now compare and contrast state of the art catalysts for CO2 electro-reduction to ethanol, all of which work at higher overpotentials with shorter activity time and have lower FE as compared to the catalyst reported here (Supplementary Table 1). For instance, Cu(100) works at \(-0.97\) V vs. RHE yielding ethanol with a FE% of 14.7\(^29\). Further, use of Cu based nano-particles in an ensemble fashion (trans-CuEn) showed a FE% of ethanol formation to be 17 at \(-0.86\) V vs. RHE\(^30\). While, with tailoring of cubic Cu nanocrystals to an edge length of 44 nm, FE% of 80 was achieved for CO2 reduction but the FE% for ethanol formation was as low as 3.7\(^31\). On the other hand, alloys like CuZn show that both the selectivity and FE% of ethanol formation can be governed by tuning the Cu:Zn ratio in the catalyst with a maximum FE% of ethanol formation 29.1 and current density (\(-3.8 \text{mA cm}^{-2}\)) obtained for CuZn at \(-1.05\) V vs. RHE\(^32\). Similarly, electrodesposition Cu–Ag alloy films (6\% Ag) exhibit a FE% of ethanol formation to be 25 at \(-0.7\) V vs. RHE with a relatively high current density of \(-300 \text{mA cm}^{-2}\)\(^33\). Electrodeposited Cu–Ag alloy films exhibit FE% of 11.8 at \(-0.88\) V vs. RHE with a current density of \(-31.2 \text{mA cm}^{-2}\)\(^34\). Materials like nanodiamonds on B and N co-doping shows a very good FE% of 93 and selectivity toward ethanol\(^10\).

With the aim to synthesize effective and stable electrocatalysts for CO2 reduction for the selective ethanol formation, we focus on a molecular Co-corrole catalyst. Metal corroles are structural similar to metal porphyrins with both the metal centers and ligands participating in multielectron redox processes and are promising candidates for efficient proton-coupled electron transfer\(^35-42\). These metal complexes stabilize radical intermediates thus providing an effective pathway to facilitate C–C step-up\(^43,44\). Cobalt and iron corroles have been previously found to be catalytically active for CO2 reduction to CO\(^35\).

We thus explore this class of catalysts for CO2 electroreduction by using cobalt triphenylphosphine 5,10,15-iris(2,5,6-tetraflouoro-4-(MeO-PEG(7))thiophenyl) corrole Co(PPh3) \((-\text{S-PEG(7)-OME})_3\) ("Co-corrole") where all the three pentafluorophenyl-groups on the corrole macrocycle renders the corrole ring electron deficient\(^45\). Chemical modification with the \(-\text{S-PEG(7)-OME}\) moieties at the para-positions of the meso-C6F5 groups was performed (Fig. 1a) to optimize anchoring and equal distribution of the catalyst on the electrode surface. The chemical synthesises and characterizations are described in detail in the methods section and in the Supplementary Information file (Supplementary Figs. 1-6). The immobilization process of Co-corrole over carbon paper is implemented via drop casting by using anacetonitrile solution of Co-corrole. The modified carbon paper electrodes are stable in aqueous solution due to the insolubility of the Co-corrole moiety in water resulting in the formation of a sustainable heterogenized catalyst with extended lifetime for electrocatalysis.

Electrochemical properties of the Co-corrole were investigated by cyclic voltammety, with glassy carbon as working electrode in CH3CN under Argon and 0.1 M TBAPF6 as supporting electrolyte. As shown in Fig. 1b, red curve, two one electron redox peaks at \(-0.5 \text{V (Co(III)/Co(II)) and } -1.5 \text{V (Co(II)/Co(I)) vs. NHE are occurring (Supplementary Fig. 7). The irreversibility of the redox peak at } -0.5 \text{V is likely due to the partial loss of the PPh3 ligand}\(^46\). In analogy to previous report by Kadish et al.\(^50\), these two couples Co(III)/Co(II) and Co(II)/Co(I) are metal centered redox processes. The reversible two one electron redox peaks at 0.73 and 1.12 V vs. NHE are ligand centered oxidations and correspond to the formation of a cationic and dicatonic cobalt(III) corrole complex\(^50\). DFT calculations suggest that the one-step and the two-step reduction at \(-0.5 \text{ and } -1.5 \text{V of the cobalt(III)-corrole leads to enhanced } \pi\text{-back bonding which strengthens the Co–N bonds and the cobalt corrole macrocycle becomes planar (Fig. 1c). Therefore, demetallation is energetically disfavored, which enables catalyst at a single Co(I)-site. The cyclic voltammetry of Co-corrole under CO2 (Fig. 1b, black
Characterization of the electrocatalyst on the electrode surface.

Cobalt triphenylphosphine 5,10,15–tris(2,3,5,6-tetrafluoro-4-(MeO-PEG(7))thiophenyl) corrole, Co(PPh₃)(TpFPC) (-S-PEG (7)-OMe)₃ ("Co-corrole"), is deposited on carbon paper (fabricated via drop casting using an acetonitrile mixture). The catalyst physisorbed on carbon paper was subjected to X-ray photoelectron spectroscopy (XPS) analysis before (Supplementary Table 2) and after the electroreduction (Supplementary Table 3). XPS survey scans exhibited the corresponding Co2p, Co3p, N1s, F1s, S2s, S2p, and P2p binding energy regions (Supplementary Fig. 15). The observed peaks correspond to Co2p, F1s, and P2p in the spectrum of Co-corroles as well as the absence of these peaks in the spectrum of non-modified carbon paper confirmed the presence of Co-corrole on the carbon paper. The high-resolution Co2p and N1s XP spectra (Supplementary Fig. 15) are in good agreement with previously published XPS data from CoTPP multilayer films.¹⁴,¹⁵

The main peak for Co 2p₃/₂ at 780.18 eV, is located at a typical cobalt(II) position (e.g., 780.2 eV for CoO) and the main peak for N1s is at 398.53 eV. Supplementary Fig. 15 displays also a C1s XP spectrum taken after electrocatalysis reaction. We observe two signals at 284.6 and 286.2 eV, because not all aromatic carbon atoms in the Co-corrole are the same, due to a lowering of symmetry to Cᵥ for corroles relative to D₄h for porphyrins. The shake-up satellite at 289.0 eV is typical for organic molecules with extended conjugated π systems. The XPS scans show that the catalyst is stable in course of electrocatalysis (Supplementary Fig. 15).

Heterogeneous CO₂ electroreduction. The heterogeneous electrochemical CO₂ reduction experiments were carried out with Co-corrole deposited on carbon paper with effective loadings of 0.2 mg cm⁻². The modified electrode was found to reduce CO₂ to ethanol and methanol in 0.1 M NaClO₄ at a potential of approximately -0.8 V vs. RHE (pH = 6.0, 0.1 M phosphate buffer, Table 1). Controlled potential electrolysis (CPE) under CO₂ of Co-corrole modified carbon paper exhibits a TON = 196 and a TOF = 0.015 s⁻¹ for the catalytic conversion of CO₂ to EtOH over 5 h (Fig. 2a–d). The quantification of products was performed using the observed ¹H-nuclear magnetic resonance (NMR)- and gas chromatography mass spectrometry (GC–MS) measurement (e.g., in Fig. 3a and Table 1, and Supplementary Notes 1–3). XPS analysis of the...
electrode materials before and after catalysis reveals that the catalyst is stable in course of electroreduction and the catalyst pertaining to the reduction process are molecular Co-corrole units (Supplementary Fig. 15). Moreover, in the course of 5 h electrolysis at \(-0.8\) V vs. RHE the Faradaic efficiency (FE%) for the ethanol production was measured at different intervals of time (Fig. 2a). Figure 2a illustrates that the FE\(=\)~48% stays constant throughout the electrocatalytic reduction process.

Subsequently, we have performed CPE with the modified carbon paper electrodes at different potentials, between \(-0.515\) to \(-0.955\) V vs. RHE for 5 h with current densities of 1.9–2.9 mA cm\(^{-2}\). \(\text{H}_2\) is the main gaseous compound and in the liquid phase ethanol, methanol, acetate, formaldehyde, glyoxal, and formate was detected. The quantifications of the respective gaseous and liquid compounds are summarized in Fig. 2b, c, Table 1, and Supplementary Figs. 16–23. During the \(\text{CO}_2\) reduction process, *deuterated ethanol derivatives*

**Table 1 Average Faradaic efficiency for each product detected on the Co-corrole-carbon paper electrode**

| Potential V vs. RHE | Total FE% | Charge passed (Coulomb) |
|---------------------|-----------|-------------------------|
|                     | CH\(_3\)CH\(_2\)OH | CH\(_3\)OH | HCOO\(^–\) | CH\(_2\)COO\(^–\) | \(\text{H}_2\) | HCOH | (CHO)\(_2\) | Avg. |
| \(-0.515\)          | 59 – 12   | – 17                  | 10 – 27         | 5 – 27         | – 20 | 3 – 26 | – 3 | 35 |
| \(-0.585\)          | 52 – 10   | 6 – 22                 | 3 – 22          | 3 – 22         | 5 – 20 | 2 – 26 | 1 | 36 |
| \(-0.650\)          | 45 – 8    | 1 – 27                 | 5 – 27          | 5 – 27         | 5 – 20 | 3 – 26 | 2 | 39 |
| \(-0.700\)          | 32 – 6    | 4 – 27                 | 5 – 27          | 5 – 27         | 5 – 20 | 3 – 26 | 3 | 40 |
| \(-0.730\)          | 23 – 5    | 4 – 27                 | 5 – 27          | 5 – 27         | 5 – 20 | 3 – 26 | 5 | 42 |
| \(-0.770\)          | 14 – 4    | 8 – 26                 | 1 – 27          | 1 – 27         | 3 – 20 | 1 – 26 | 1 | 43 |
| \(-0.800\)          | 8 – 10    | 10 – 28                | 3 – 28          | 3 – 28         | 1 – 20 | 1 – 26 | 3 | 44 |
| \(-0.855\)          | 5 – 12    | 12 – 33                | 2 – 23          | 2 – 23         | 1 – 20 | 1 – 26 | 2 | 47 |
| \(-0.905\)          | 3 – 12    | 12 – 37                | 1 – 27          | 1 – 27         | 1 – 20 | 1 – 26 | 1 | 50 |
| \(-0.955\)          | 2 – 13    | – 36                   | – 36            | – 36           | – 36 | – 36 | – 36 | 53 |

*In 0.1 M NaClO\(_4\) (0.1 M pH = 6.0 phosphate buffer)*

**Fig. 2** a Constant potential electrolysis of electrochemical \(\text{CO}_2\) reduction by the Co-corrole modified carbon paper electrode at a potential of \(-0.8\) V vs. RHE (black curve), Faradaic efficiency for ethanol production over 5 h electrolysis (blue rectangles). b FE\% vs. potential plot for potential dependent product formation. c FE\% vs. potential plot for minor formed formaldehyde and solvated dimer of formaldehyde at different potentials. The error bars represent standard deviation of six measurements (three electrochemical reactions with two product analysis measurements for each reaction). d MS spectra obtained after electrolysis at \(-0.8\) V vs. RHE in \((1:3)\) D\(_2\)O/H\(_2\)O 0.1 M NaClO\(_4\) saturated with \(\text{CO}_2\).
**Fig. 3**  
(a) $^1$H-NMR spectrum of the electrolyte after 5 h of CO$_2$ electrolysis over Co-corrole-carbon paper electrode at $-0.585$, $-0.7$, $-0.8$, and $-0.905$ V vs. RHE in 0.1 M NaClO$_4$, pH = 6, phosphate buffer, and phenol as the internal standard in DMSO.  
(b) $^{13}$C-NMR (101 MHz, H$_2$O:D$_2$O = 5:1) of the electrolyte after 5 h of electrolysis at $-0.8$ V vs. RHE in $^{13}$CO$_2$, 0.1 M NaClO$_4$, pH = 6, phosphate buffer.  
(c–f) GC–MS spectrum of the electrolyte after bulk electrolysis at $-0.8$ V vs. RHE in $^{12}$CO$_2$ and $^{13}$CO$_2$: c $^{13}$C enriched ethanol, d $^{12}$C enriched ethanol, e $^{12}$C enriched methanol, and f $^{13}$C enriched methanol.  
(g) SEC-FTIR spectra during the CO$_2$ reduction with 20 mM Co-corrole in 0.1 M TBAPF$_6$ (in CH$_3$CN/H$_2$O = 4:1), at potentials from $-0.3$ to $-1.9$ V vs. NHE.
the FE% for ethanol was found in the range of 9–48 with the selectivity for C₂ over C₁ increasing with increase in the applied cathodic potential from −0.73 to −0.96 V vs RHE with a significant decrease in methanol production. CPE long-term measurements were performed at −0.73 V (pH = 6.0) and −0.70 V (pH = 7.2) vs. RHE, where the activity of the Co-corrole modified carbon electrodes retained for 140 h (Supplementary Figs. 8–13).

To further trace the origin of methanol and ethanol, we carried out CO₂ reduction experiments with a D₂O/H₂O mixture. Deuterium distribution during the CO₂ reduction process was monitored by conducting electrolysis at −0.8 V vs. RHE in D₂O/H₂O (1:3). After electrolysis, the mass spectra indicated the formation of reduced product and the following peaks appeared—m/z of 45–52 (Fig. 2d). Among the peaks obtained, the one with m/z value 52 (CD₄CD₂OD) can be assigned for hexa-deuterated ethanol. In the spectrum apart from the molecular ion peak, there are also peaks corresponding to other fragments with m/z = 50 which can be from CD₃CD₂O and m/z = 34 for CD₂OD− which are characteristic fragments of CD₂CD₂OD. This deuterium further proves that the source and incorporation of protons in the reduced product is from the solvent and the source of ethanol is from CO₂ reduction. To confirm the source of carbon in the reduction products, we have conducted the reduction experiments with ¹²CO₂ and ¹³CO₂. The ¹H and ¹³C-NMR spectra after CO₂ reduction at the Co-corrole modified carbon paper electrode exhibit resonances for ethanol, methanol, acetic acid, and formic acid (Fig. 3a, b). The ¹³C-NMR spectrum after the reduction of ¹³CO₂ clearly indicates four doublets at 58.3 ppm (J_CCC,EtOH = 37.5 Hz), 17.6 ppm (J_CCEtOH = 37.5 Hz), 176.4 ppm (J_CC,acetic acid = 56.2 Hz), and 20.7 ppm (J_CC,acetic acid = 56.2 Hz) indicating the reduction of ¹³CO₂ and formation of C-C bond (Fig. 3b). HCOOH and CH₃OH appear as singlets at 170.0 and 49.8 ppm in the ¹³C-NMR spectrum (Fig. 3b), respectively. These results were further substantiated by GC-MS data, which shows a shift of m/z = 2 for the molecular ion peak of CH₂CH₂OH on ¹³C enrichment (Fig. 3c, d). The results for CH₂OH⁺, when compared to ¹²CO₂ reduction shows a shift by m/z = 1 (Fig. 3e, f). On analysis of the fragmentation patterns, we observe that for ethanol obtained by the reduction of ¹²CO₂, the peak at m/z = 29 corresponds to the CH₃CH₂⁺ ion. On the other hand, when ¹³CO₂ is used, the peak occurs at m/z = 31, which is due to the substitution of both ¹²C centers with ¹³C isotopes. Likewise, the peak obtained at m/z = 31 in case of ¹²C enriched ethanol resembles the CH₂OH⁺ fragment which on ¹³C enrichment shifts to m/z = 32. For ¹³C enriched methanol, the peak at m/z = 15 resembles CH₃⁺ ion which shifts to m/z = 16 on ¹³C enrichment. The results obtained from both the ¹³C-NMR and GC-MS experiments prove that the source of ethanol as well as methanol is CO₂ (Fig. 3b–f).

Spectro-electrochemical Fourier-transform infrared spectroscopy (FTIR) measurements (SEC-FTIR) at applied potentials of −0.3 to −1.9 V vs. NHE, illustrated in Fig. 3g exhibit increasing IR bands at 3400 cm⁻¹ (O–H stretching), 2860 cm⁻¹ (C–H stretching), 2850 cm⁻¹ (C–H stretching), 1100–1060 cm⁻¹ (C–O stretching), indicating the stepwise increase of [alcohol/acid] formation. The IR-band at 1640 cm⁻¹ (C = O stretching of HCOO⁻) indicates the formation of a dicarbonyl species. The corresponding IR bands for CO₂ at 2360 and 2340 cm⁻¹ (C = O stretching of CO₂) decrease during the reaction, indicating that CO₂ is converted under these conditions.

Discussion

An in-depth elucidation of the mechanistic pathway of the reduction process is beyond the scope of this present work. Detailed investigations are underway in our laboratories. To increase the CO₂ reduction efficiency and to avoid hydrogen evolution at low-pH values, all experiments were performed under weak acidic conditions (pH = 6.0, 0.1 M phosphate buffer). CO₂ reduction under heterogenized conditions with Co-corrole modified carbon electrodes exhibits a redox couple being [Co-corrole]¹⁺/[Co-corrole]²⁺, which was found to be at −0.8 V vs. RHE. This markedly resembles the redox behavior of the Co-corrole molecule in the solution, so the redox properties are unperturbed upon heterogenization. We thus propose the molecular characteristics of the electrocatalyst to be persistent upon heterogenization. The EPR spectrum obtained after electrochemical reduction and subsequent dosage of CO₂ at room temperature exhibits a rhombic S = 1/2 signal at g = 2 with a weak ⁵²Co hyperfine splitting and indicates the formation of Co(III)–CO₂⁺⁻ species (Supplementary Fig. 24).

The role of protons is extremely crucial in this work and sets this process apart from related CO₂ reduction processes. For instance, at pH = 6.0 the necessary protons are provided for the subsequent proton coupled electron transfer (PCET), due to this, reduction to methanol/ethanol takes place (Fig. 3a). By performing the same experiment at pH = 7.2, we experimentally observe the reduction of CO₂ to a mixture of formaldehyde, ethanol, methanol, acetate, and formate (see assignment of NMR resonances in the supplementary Fig. 20), and at a pH = 8.0 we detect only CO as the main reduction product (Supplementary Fig. 25a–c and Supplementary Notes 4, 5). This implies that the rate of PCET drastically decreases at weak to moderately basic pH values. For the successful chemical transformation of CO₂ to methanol and ethanol, this result is crucial in the present context.

The existence of the Co(III)–CO₂⁺⁻ can only be justified through the presence of CO₂⁺⁻ formed at a very high potential of ca. −1.5 V vs. RHE. In our case, the reduction wave at ca. −0.8 V vs. RHE is responsible for the CO₂ reduction. This implies that the Co(I) in the center of the corrole complex enables the reduction of CO₂ to the CO₂⁺⁻ intermediate at a lower cost of energy.

We suggest a mechanism similar to that proposed by Koper et al., which is illustrated in Fig. 4. The reaction follows a low energy pathway where the carboxyhydroxyl intermediate gets simultaneously reduced by 1 e⁻, gets protonated to form a HCOO⁻ intermediate and can be detected by ¹H-NMR spectroscopy (Fig. 3a, Supplementary Table 4, and Supplementary Notes 6–8). The HCOO⁻ intermediate further undergoes 1 e⁻ reduction with the elimination of OH⁻ to give HCO⁺ stabilized at the Co(III) site. Low potential for reactivity then drives the reaction toward methanol. This reduction pathway of HCO⁺ to CH₃OH at the cobalt site is in accordance with the mechanism reported by Koper et al. On the other hand, at a higher potential (>−0.73 V vs. RHE) an increased concentration of HCO⁺ is developed and the reaction takes a second route with the recombination of two formyl radicals (Co(III)–HCO⁺, HCO⁺) leading to oxaldehyde intermediate (OHC–CHO). OHC–CHO was previously reported to be a precursor for the formation of ethanol as well as a key intermediate for C–C step-up leading to C₂ products. The π-conjugation present in OHC–CHO inherently makes it prone to reduction giving OCH═CHO which subsequently reduces to OCH═CH₂OH which further reduces to CH₂CHOH. The high selectivity for alcohol is due to the formation of the HCO⁻ intermediate which is readily reducible to methanol. In the case of ethanol, we believe the formation of oxaldehyde intermediate opens up a more favorable route to form ethanol.

The proposed reaction pathways for the formation of the methanol and ethanol were further substantiated by conducting reduction studies of possible intermediates like formic acid, formaldehyde, methanol, and glyoxal under the same reaction conditions reported for Co-corrole–carbon paper electrodes. To
test this conjecture, further reduction of the $2e^-$ reduced product formic acid was induced, where it yielded a mixture of methanol and ethanol which indeed implies formic acid to be an important intermediate. Cyclic voltammetric measurements show an increase in current density (Supplementary Fig. 34a) upon the addition of 10 mM of formic acid. CPE was performed at $-0.73 \text{ V vs. RHE}$ over Co-corrole–carbon paper electrode for 5 h and the products obtained were analyzed in GC–MS spectrum where the presence of the characteristic peaks of methanol ($m/z = 32$) and ethanol ($m/z = 46$) were observed (Supplementary Figs. 36–38). The obtained results were further confirmed by $^1\text{H}-\text{NMR}$ spectroscopy (Supplementary Fig. 34b). The proposed HCOOH intermediate under the low potential of reactivity gets reduced to HCHO and methanol, which are the final products and does not get further reduced. To verify the role of oxaldehyde in the current mechanistic cycle, 0.1 mM OHC–CHO was externally added under the reaction condition and $\text{CH}_2\text{CH}_2\text{OH}$ was obtained proving oxaldehyde to be a key intermediate for $\text{CH}_3\text{CH}_2\text{OH}$ formation (Supplementary Fig. 35a, b). The high selectivity for alcohol is primarily due to the formation of the formic acid intermediate followed by formation of HCO$^\bullet$ intermediate which is readily reducible to methanol. In the case of ethanol, we believe the formation of oxaldehyde is due to coupling of two HCO$^\bullet$ intermediate which opens up a more favorable route to form ethanol. To complete the studies, we performed comparative measurements with two similar Co-corroles (cobalt triphenylphosphine 5,10,15-tris(pentafluoro-phenyl) corrole (PPh$_3$-CoTpFPC) and cobalt triphenylphosphine 5,10,15-triphenyl corrole PPh$_3$-CoTPC)), which consist of (a) three meso- C$_6$F$_3$- groups or of (b) three meso- C$_6$H$_3$- groups. The results are illustrated in the Supplementary Informations file of the paper (Supplementary Fig. 43). The main reduction products under the same reaction conditions at pH = 6 were assigned to formic acid, methanol, and acetic acid. Only trace amounts of ethanol were found employing these two catalyst systems.

To conclude, we have demonstrated the electrochemical reduction of CO$_2$ to ethanol and methanol with a Co-corrole–carbon paper electrode at a low potential ($-0.8 \text{ V vs. RHE}$) with a FE of 48% over a time period of 5 h. The Co-corrole–carbon paper electrode can withstand extremely high operational time of up to 140 h marking the highest efficiency for a molecular electrocatalyst reported so far in the literature. This is accomplished by the formation of a OHC–CHO type intermediate using a MeO-PEG(7)-S-modified cobalt corrole molecular catalyst. The Co-corrole molecule tend to stabilize different radical intermediates at the metal site. Thus, when reacted with a greater number of electrons highly reduced products are formed. On simulating the reactivity of Co-corrole, we found both experimentally and theoretically that in contrast to the CO pathway our catalyst proceeds via a formic acid pathway. By applying a redox potential of $-0.73 \text{ V vs. RHE}$, a mixture of methanol and ethanol is detected. The obtained reaction products can only be explained if formic acid is developed temporarily, which is subsequently reduced to the formyl radical (HCO$^\bullet$). The HCO$^\bullet$ forms methanol as well as glyoxal and ultimately the glyoxal is then reduced to form ethanol serving our catalyst to operate at a low over potential.

**Methods**

**Chemicals.** All chemicals and solvents were commercially available and were used as obtained, unless otherwise noted. High-performance liquid chromatography grade solvents were used in all the experiments with water, methanol, acetonitrile, and sodium perchlorate (NaClO$_4$) purchased from Merck, tetrabutylammonium perchlorate (Bu$_4$NPF$_6$), 98%, purchased from Alfa Aesar, was twice recrystallized with absolute Ethanol, dried under high vacuum and stored under nitrogen. The 5,10,15-tris(pentafluoro-phenyl)corrole was synthesized.
at 25 °C. The pH value of the solutions were obtained using a EUTECH pH 510 pre-calibrated with thermo Scientific pH 4.01, 7.0, and 10.01 buffer solutions. For all the measurements CO₂ was continuously purged into the solution. All the potentials are represented in RHE scale with iR correction.

For electrochemistry in non-aqueous medium, acetonitrile was used as the solvent of choice with a similar electrochemical setup with glassy carbon as the working electrode, Ag/AgCl (0.1 M KCl) as the reference and Pt wire as the counter electrode with 0.1 M tetraethylammonium perchlorate or 0.1 M tetraethylammonium hexafluorophosphate as the electrolyte. Under this electrochemical conditions, the redox behavior of 0.1 M ferrocene in acetonitrile was studied, which was further used as the internal standard.

**Detection and quantification of the CO₂ reduced products.** ¹H- and ¹³C-NMR spectroscopy of the carbon dioxide reduced liquid products were recorded on a Bruker Ascend 700 MHz Avance III NMR spectrometer equipped with a cryoprobe and a JEOL ECS-400 NMR spectrometer. As internal standard, 20 mL aqueous solution of 20 mM phenol and 10 mM of dimethyl sulfoxide were used. After CPE, to 350 μL electrolyte, 200 μL D₂O, and 30 μL of the internal standard were added and transferred into a NMR-tube. During the measurements, the water peak was suppressed to increase the signal intensity of the anaytes. The CO₂ reduced products were further analyzed using GC–MS. Trace 1300 GC and ISQ QD single quadruple GC–MS instrument with a TG-5MS capillary column (30 m × 0.32 mm × 0.25 µm) supplied by Thermo Fisher Scientific and DB–624 capillary column (30 m × 0.25 mm × 0.25 µm) supplied by Agilent were used for the same. For gaseous analysis Carboplot 007 capillary column (25 m × 0.53 mm × 0.25 µm) supplied by Agilent was used for separation and TCD for detection.

**Electrochemically active surface area (ECSA) calculation.** ECSA value is obtained by using the following equation

\[
\text{ECSA} = \frac{C_{\text{ele}}} {C_{\text{Co}}}
\]

where \(C_{\text{ele}}\) = electrochemical double layer capacitance which is obtained from the slope of the current vs. scan rate plot in the non-Faradaic region and \(C_{\text{Co}}\) = specific capacitance of the sample and in this case, \(C_{\text{Co}} = 0.040 \text{ mF cm}^{-2}\). ⁵⁵

**Analysis of the CO₂ reduced products in ¹H-NMR and GC–MS.** Compounds formed at different potentials were detected directly by '¹H-NMR (integrated with respect to DMSO (δ = 2.73 ppm as internal standard) with a triplet signal at δ = 3.07 ppm) and with a quartet signal at δ = 3.67 ppm indicating ethanol (Supplementary Fig. 17); a singlet at δ = 3.37 ppm showing the presence of methanol (Supplementary Fig. 17).

For detection of formaldehyde, 2 mL of the reaction mixture was taken in a 20 ml Headspace vial with 0.1 M ethanol and was acidified with 100 µL 1% p-toluenesulfonic acid. This mixture was then heated at 60 °C for 1 h and then GC–MS measurements were done⁵⁶. In the mass spectrum, peak centered at m/z = 104 represents diethoxymethane indicating the formation of formaldehyde with a retention time around 3.00 min (Supplementary Figs. 39 and 40). Glyoxal was detected in the spectrum at m/z = 58 with a retention time of 3.35 min (Supplementary Figs. 41 and 42).

**XPS measurements.** XPS was performed by using a Theta Probe, Thermofisher, UK, using monochromatic Al K X-rays (hν = 1486.6 eV), spot size 400 microns and with a photoelectron take-off angle of 90° with respect to the surface plane. The binding energies were corrected using the C1s peak at BE = 284.6 eV that arises from adventitious hydrocarbon.

**Data availability**

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Received: 3 December 2018 Accepted: 8 August 2019 Published online: 27 August 2019

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program (project M00146, "RERI-uasb"). W.S. and S.G. thanks Dr. Markus Himmelsbach for the ESI-MS measurement. P.G. thanks the Fonds of the Chemical Industry for a PhD fellowship. U.-P.A. is grateful for support by the Deutsche Forschungsgemeinschaft (Emmy Noether grant, AP242/2-1; AP242/6-1) and the Fraunhofer Internal Programs under Grant no. Attract 097-602175. U.-P.A. and P.G. were funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation—Germany’s Excellence Strategy, EXC-2033—Project number 390677874).

Author contributions
W.S. and S.R. conceived the project and wrote the paper. W.S., S.G., F.P. and M.H. developed and carried out the syntheses of metal corroles, analytics, and optical characterization. S.P., S.G. and R.D. conducted all electrochemical measurements, experiments with CO2 reduction, and GC–MS characterizations. W.S., S.G. and S.B. carried out the NMR experiments. S.S.S. did modeling and calculations. U.-P. A. and P.G. performed the SEC-FTIR experiments and the analysis of gaseous products after heterogeneous catalysis. A.A., H.C. and P.S. performed additional long-time electrochemical measurements. S.M. performed the ESR measurements. W.S. and S.R. supervised and coordinated the work. All authors have given approval for the final version of this paper.

Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-019-11868-5.

Competing interests: The authors declare no competing interests.