Highly selective electrochemical reduction of carbon dioxide using Cu based metal organic framework as an electrocatalyst

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ABSTRACT

The electrocatalytic reduction of carbon dioxide at Cu based metal organic framework film surface was studied in N,N-dimethylformamide containing tetrabutylammonium tetrafluoroborate with saturated CO_2. Cyclic voltammetric studies of the MOF film immobilized onto GC in 0.1 M KCl clearly showed the well defined Cu(II)/Cu(I) and Cu(I)/Cu(0) reversible redox responses. In the presence of saturated CO_2/TBATFB/DMF solution, the cyclic voltammetric studies revealed that the electrochemically generated Cu(I) formed adduct with carbon dioxide in-situ and on further formed oxalic acid. The formation of oxalic acid was confirmed by GCMS in bulk electrolysis experiment. A detailed mechanism for the formation of oxalic acid was also discussed in this communication.

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1. Introduction

Metal organic framework, one of the porous materials has crystalline ordered structure, extra high porosity, high thermal stability and adjustable chemical functionality that is capable of storing CO_2 [1–3]. The open polyhedral secondary building block units contained MOFs that exhibit very high gas adsorption capacities for H_2, CO_2 and CH_4, and due to mesocages provide the enormous open space for pore volumes. Yaghi et al., report the highest amount of CO_2 uptakes (2400 mg g^{-1} at 298 K and 60 bar) and H_2 uptakes (176 mg g^{-1} at 77 K and 70 bar) by Zn-MOF materials [4]. Recently Jian-Rong et al., reported that the total pore volume and surface area of MOFs are directly proportional to the amount of CO_2 adsorption [5].

Conversion/sequestration of CO_2 to smaller useful organic molecules has become an important issue, because increment of CO_2 level in the atmosphere leads to adverse impact on the environment. Recent research on CO_2, mainly focused on electrochemical conversion and fixation of CO_2 and has been reviewed in modern synthetic organic chemistry. Previous studies are reported on the conversion of CO_2 into formic acid, methane, ethane, ethylene, propylene, methanol and ethanol under different electrocatalytic conditions in different solvents [6,7]. Several methods are adopted for conversion

and activation of CO_2 such as chemical, thermochemical, photochemical, biochemical, electrochemical and hydrothermal methods [8,9]. Among these, electrochemical method is an attractive technique, due to its simple procedure and ambient operation conditions. The electrochemical reduction of CO_2 occurs by the abstraction of proton from the solvents and yields various products [10]. In recent years many investigators have studied the electrochemical reduction of CO_2 on metallic electrodes and modified electrodes in aqueous, non-aqueous and ionic liquid medium at various temperatures [11,12]. Particularly copper has been widely investigated for electroreduction of CO_2 in protic and aprotic solvents like dimethylsulphoxide, N,N-dimethylformamide, propylene carbonate, methanol and acetonitrile [7]. In non-aqueous medium, two competitive reaction pathways have been described; i) lead to the formation of oxalate anion by 2-electrons reduction and dimerization and ii) proceed through nucleophilic coupling of CO_2^- radical anion with $CO_{2(ads)}$ and formed CO and CO_3^{2-} [13].

Metal organic frameworks have unique properties like high surface area (500–6240 m^2 g^{-1}), wide range of pore size (3–3.5 A°), pore volume (0.4–3.6 cm^3 g^{-1}) and a variety of functionalities [4], these make a good catalytic material for a number of organic reactions. MOF could be functionalized with a variety of organic linkers, responsible for the many catalytic organic reactions. Although a large number of MOFs have been examined as heterogeneous catalyst [14], particularly MOFs with carboxylate linkers have high surface area and wide range of pore size with much attention to catalytic reactions. In this communication we demonstrate the uniform film of $Cu_3(BTC)_2$ on GC (MOF film) as an efficient electrocatalyst for the selective reduction of carbon dioxide.

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2. Experimental

2.1. Experimental procedure

Cu$_3$(BTC)$_2$ was synthesized electrochemically using the procedure reported by us, described as [15], two copper electrodes having similar area (10.5 cm^2) were used as anode and cathode. Electrolysis was carried out in an electrochemical cell under constant voltage electrolysis using the organic linker (0.1 M BTC) and supporting electrolyte (TBATFB) in 50 ml methanol solution for 360 min. Finally the sky blue color precipitate of Cu$_3$(BTC)$_2$ was collected from the electrolysis cell and allowed to dry in a hot air oven at 120 °C for 12 h and activated at 200 °C for 2 h. The yield of the product corresponding to the amount of weight loss in the anode is 97.51%.

The cyclic voltammetric experiments and bulk electrolysis were performed using BAS IM6 Electrochemical Analyzer (USA). In a single compartment conventional three electrodes system, glassy carbon and a platinum foil were used as the working and counter electrodes, respectively. All potentials were recorded against SCE or Ag/Ag$^+$ reference electrode. The Cu$_3$(BTC)$_2$ ink was prepared in acetone with Nafion solution under ultrasonic condition. The electrochemically synthesized Cu$_3$(BTC)$_2$ was coated on glassy carbon electrode surface by drop dry method.

2.2. Electrocatalysis

The bulk electrolysis was carried out in a 5 ml (carbon dioxide saturated in 0.01 M TBATFB/DMF) batch in a three electrode single compartment electrochemical cell, by applying a constant potential of about −2.5 V vs Ag/Ag$^+$ for 10 min. During the course of the experiment and after electrolysis an aliquot was taken out, FT-IR and GCMS experiments were carried out to monitor the formation of the products.

3. Results and discussion

The synthesized material phase purity was characterized by powder XRD pattern (Fig. 1a). The diffraction peaks of electrochemically synthesized sample are well consistent with available literature [16] and the simulated pattern published by Chui et al. [17]. The observed XRD peaks which are very sharp indicate the highly crystalline nature

of the synthesized material. These peaks correspond to the face centered cubic structure of Cu$_3$(BTC)$_2$ nanoparticles [18]. Moreover, it is interesting to note that the synthesized Cu$_3$(BTC)$_2$ from optimized experimental condition does not exhibit any peaks corresponding to CuO (2θ = 35.5 and 38.7°) or Cu$_2$O (2θ = 36.43°) and also in particular there is no significant impurities peak at 2θ = 11.0° [19] as observed by Hartmann et al. who synthesized Cu$_3$(BTC)$_2$ by hydrothermal method which confirms that higher purity Cu$_3$(BTC)$_2$ was obtained from the present method using optimized electrochemical experimental conditions.

Morphological studies clearly show that the synthesized Cu$_3$(BTC)$_2$ is highly porous in nature and higher magnification of the SEM image exhibits a uniform decoration of cubic shaped particles. TEM analysis used to find out the individual particle size of the cubic structure of Cu$_3$(BTC)$_2$ is shown in Fig. 1b. Inset in the TEM image of Fig. 1c shows the SAED pattern, in which the bright circular rings correspond to the (220), (222) and (400) planes that represent the highly crystalline nature of the synthesized Cu$_3$(BTC)$_2$ particles, which is in good agreement with the XRD results [18]. As can be seen in the TEM image, Cu$_3$(BTC)$_2$ particles are cubic shaped with sizes which are found to be in the range of 10–20 nm.

Electrochemical response of Fe-BTC was recently demonstrated by Frank et al., and they proposed a mechanism based on a MOF surface confined hydrous iron oxide film [20]. Cyclic voltammetric responses of Cu$_3$(BTC)$_2$ coated on GC electrode are crucial in order to find out the electrochemical stability of the compound and are compared with CV response of Cu foil or Cu deposited electrode (from acidified CuSO$_4$ solution (pH = 2.3)) in 0.1 M KCl at a scan rate of 20mVs^{-1} under nitrogen atmosphere illustrated in Fig. 2. In general a good experimental reproducibility indicates the mechanical stability of the frame work structure. The resulting cyclic voltammogram (Fig. 2a) shows distinct redox peak potentials at −0.14 and +0.02 V vs SCE indicating the reversible oxidation and reduction of Cu$^{(II)}$/Cu$^{(I)}$ [21]. Another reduction peak at −0.45 V vs SCE and corresponding sharp oxidation peak at −0.102 V vs SCE indicate the redox couple of Cu$^{(0)}$ to Cu$^{(I)}$. The cyclic voltammetric response of Cu$_3$(BTC)$_2$ indicated that the copper is in the Cu^{2+} ionic state which is consistent with XPS and XRD results, where as such a redox peak behavior was not observed for Cu electrode in 0.1 M KCl solution (Fig. 2a inset). The stability of the Cu$^{(II)}$ and Cu$^{(I)}$ form is very important in catalysis and will be discussed later.

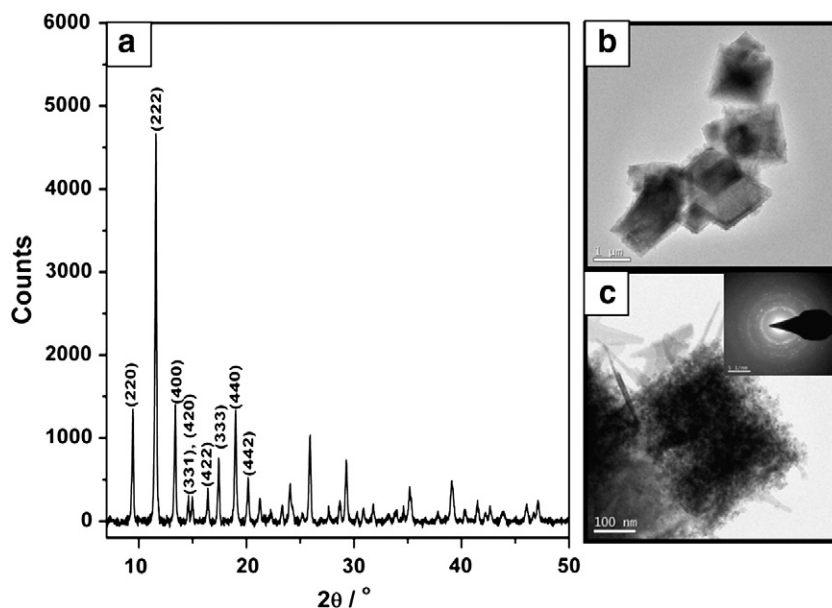**Fig. 1.** a) Powder X-Ray diffraction pattern, TEM image of b) lower and c) higher magnification, SAED pattern (inset) of Cu$_3$(BTC)$_2$.
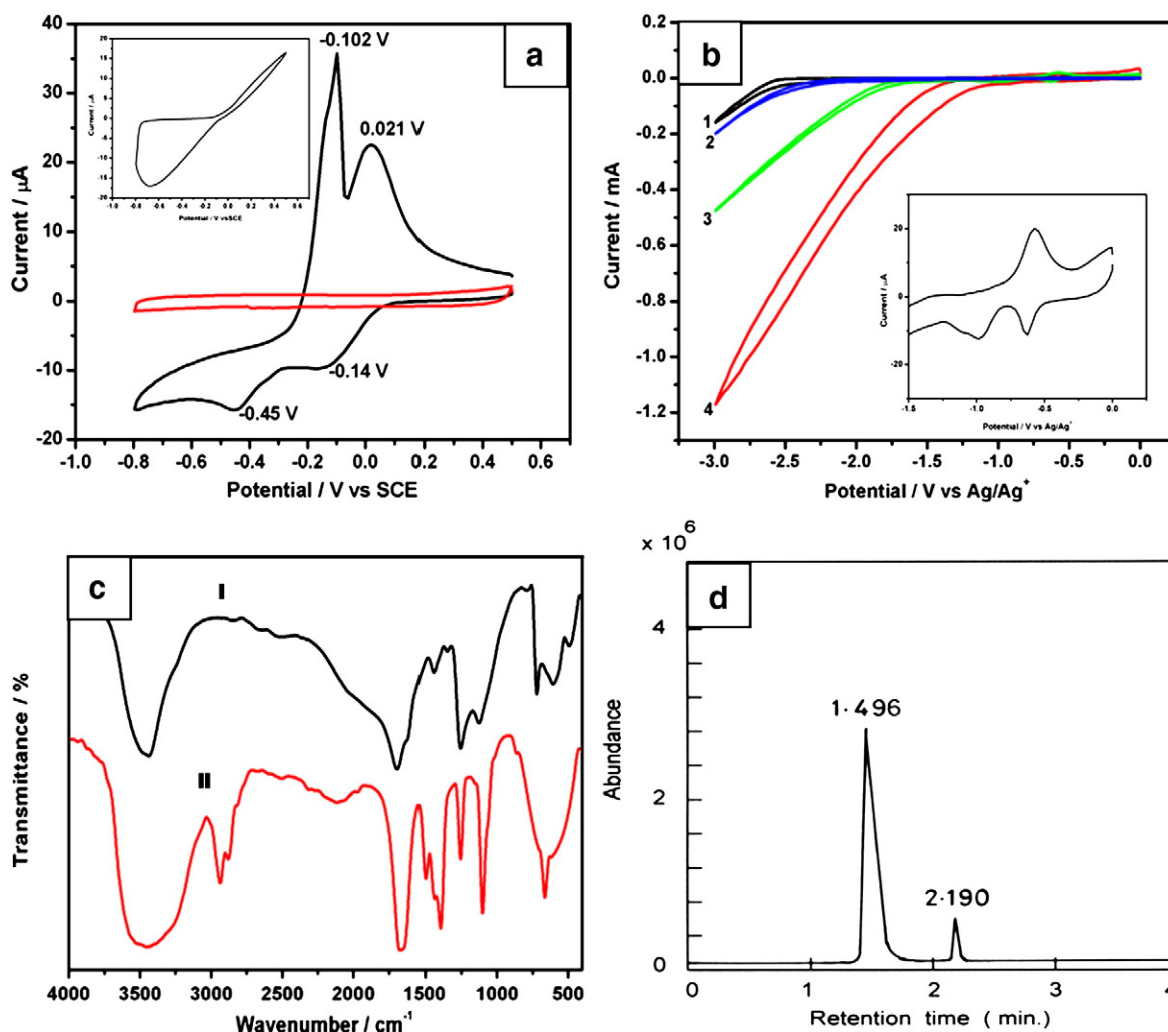
Fig. 2. Cyclic voltammogram for a) $Cu_3(BTC)_2$ coated GC (redline represents GC background), b) cyclic voltammogram 1) bare GC, 2) bare GC in presence of CO_2, 3) $Cu_3(BTC)_2$ coated GC and 4) $Cu_3(BTC)_2$ coated GC in presence of CO_2, in a solution containing 0.01 M TBATFB/DMF, scan rate 50 mVs^{-1} and c) FT-IR spectra of I) oxalic acid (authentic) and II) oxalic acid (synthesized), d) GC–MS spectrum of the bulk electrolysis product of CO_2 at $Cu_3(BTC)_2$ coated electrode surface.

So far, most of the studies discussed in literature on MOF have focused on gas adsorption with particular emphasis on molecular hydrogen, methanol and carbon dioxide, and to date, there are no reports available on electro-reduction of carbon dioxide [22]. Herein we demonstrate for the first time that the electrochemically synthesized $Cu_3(BTC)_2$ exhibits catalysis towards sequestration as well as electro reduction of CO_2 simultaneously. While bubbling the CO_2 through DMF solution for several minutes, no precipitate was formed indicating the absence of any reaction with DMF. The maximum concentration can be built to 0.199 M in DMF solution [23]. Therefore, CO_2 can be considered to be physically dissolved, i.e., under intact form in the DMF/TBATFB solution.

Since, Cu and $Cu_3(BTC)_2$ coated electrodes are behaving differently as indicated in the CV studies, here we have compared current potential response of GC and $Cu_3(BTC)_2$ coated GC electrodes in both solution without CO_2 (1 and 3 respectively) and the CO_2 saturated DMF containing TBATFB solution (2 and 4 respectively) and presented in Fig. 2b. As can be seen from cyclic voltammograms, the direct reduction potential of CO_2 starts at potential more positive in $Cu_3(BTC)_2$ coated GC electrode (-1.12 V vs Ag/Ag$^+$) than bare GC electrode (-1.75 V vs Ag/Ag$^+$), i.e potential shifts to less anodic side and also cathodic evolution current density is increased from 2.27 mAcm^{-2} to 19.22 mAcm^{-2}. This clearly indicates that carbon dioxide reduction at

the electrode is the main electrochemical process at these potentials and also brings out the electrocatalytic activity behavior of $Cu_3(BTC)_2$ on CO_2 reduction. This may be due to the tendency of absorbing more CO_2 in the pores of $Cu_3(BTC)_2$ and there is a possibility of reducing the compressed gas inside the pores electrochemically via heterogeneous electron transfer between $Cu_3(BTC)_2$ and CO_2 molecule. Further it is also proved that the catalytic activity of the Cu(II)-complex might be attributed to their immediate reduction to Cu(I) species. As in the case of CO_2 reduction using cobalt(I) complex, provided as an intermediate and a five-coordinate Co(I)–CO_2 adduct which was isolated from the reaction [24], here activated Cu(II)-MOF present as four coordinated, which is acting as a Lewis acid and forms adduct with CO_2. Hydrogen bonding between the coordinated CO_2 inside the MOF pores is important in stabilizing the adduct. Cu(I) which is formed at potential -0.62 V vs Ag/Ag$^+$ in the CO_2 saturated DMF solution is catalyzing the reduction [25] (inset of Fig. 2b). In literature, two main competitive reaction pathways have been described for the reduction of CO_2 in non-aqueous media [13]. The mechanism of reduction, resulting in oxalate anion by dimerization of CO_2^- formed from the 2-electrons reduction of CO_2.

As a first report, herein we demonstrate that the synthesized Cu based MOF as a uniform film on GC electrode electrochemically reduces CO_2 saturated DMF solution in the presence of supporting

electrolyte to oxalate anion through the formation of carbon dioxide radical anion. This oxalate anion abstracts proton from solvent to form the oxalic acid. FT-IR spectrum taken during the course of reaction confirmed the formation of oxalic acid (Fig. 2c). The resultant spectrum was also compared with that of oxalic acid (commercial sample) and was consistent. From the bulk electrolysis, the conversion and product selectivity of CO_2 to oxalic acid was also confirmed through GCMS analysis (Fig. 2d) and the peaks at 1.496 and 2.19 min correspond to oxalic acid and dissolved CO_2 respectively. GCMS study clearly confirms the formation of oxalic acid with 90% purity, and the Faradaic efficiency was calculated as 51%.

Further studies are in progress to correlate the porosity, pore volume, amount of adsorption of CO_2 in MOF with the amount of reduction of CO_2.

4. Summary

(1) Electrochemically synthesized Cu-BTC is porous in nature, is having surface area of 1498 $m^2\ g^{-1}$ and its crystalline size is 200–500 nm.
(2) Its continuous film formed on GC shows electrochemically active Cu(I) species formation.
(3) This Cu(I) forms adduct with carbon dioxide and electrochemically forms oxalic acid, which is confirmed through bulk electrolysis and analysis using GCMS.

Acknowledgments

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