

Research Article

Electrocatalytic Study of Carbon Dioxide Reduction By Co(TPP)Cl Complex

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Carbon dioxide (CO₂) is notorious for being a greenhouse gas and is the most important cause of global warming. However, it can be converted into useful products as it is a source of carbon. Reduction of CO₂ is therefore an attractive research topic for many chemists. Different methods of electrocatalytic reduction of CO₂ have been reported previously. Since CO₂ is very stable, the direct electroreduction of CO₂ into CO requires high potential at -2.2 V versus Ag/AgCl. In this work, CO₂ reduction was carried out by the photoelectrocatalysis of CO₂ in the presence of cobalt(III)tetraphenylporphyrin [Co(TPP)Cl] at -1.85 V with a current efficiency of 71%. At illuminated p-type silicon photocathode, the reduction of CO₂ into CO was performed at a potential of 300 mV which is positive. However, at the same conditions, potential of -1.55 V with a current efficiency of *ca* 65% is required for the carbon electrode.

1. Introduction

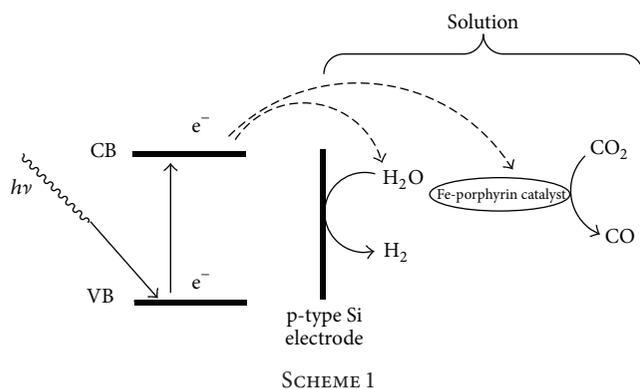
The increasing amount of carbon dioxide (CO₂) over the past years may affect the environment adversely due to the fact that it is a greenhouse gas and can lead to global warming. In the air, CO₂ is a final product of combustion of carbon-containing compounds and represents fully oxidized carbon. It is thermodynamically very stable and it requires a lot of energy to break its C-O bonds. However, there are four different methods for CO₂ splitting: enzymatic [1, 2], electrochemical (electrocatalytic) reduction [3, 4], photoreduction [5, 6], and abstraction of an oxygen atom from a CO₂ molecule by coordination complexes [7]. The conversion of CO₂ into valuable products is challenging as it requires a lot of energy [8–10]. Photosynthesis, photocatalytic, and electrochemical reduction of CO₂ are the effective processes to use CO₂ as a carbon source and convert it into useful products. Energy is required for all these processes, such as requirement of electricity in electrochemical reduction process [11]. CO₂ has been converted into chemicals (such as formic acid) and fuels (such as methanol, methane, and carbon monoxide (CO)) previously [12–14]. Photochemical conversion of CO₂ to fuels or valuable chemicals using

renewable solar energy can decrease the amount of CO₂ in the atmosphere [15].

Recycling atmospheric CO₂, by its capture and subsequent reduction to valuable products and liquid fuels, is an increasingly important research area. It is possible to drive the half-cell reaction ($\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$) under visible light illumination at a p-type silicon (p-Si) photocathode using a catalyst [16, 17].

A light assisted generation of syngas (H₂ : CO = 2 : 1) from CO₂ and water can be achieved by using p-Si/catalyst. In the system, water is reduced heterogeneously on p-Si surface and CO₂ is reduced homogeneously by the catalyst (Scheme 1) [17, 18].

The field of electrocatalytic reduction of CO₂ by metal complexes has been studied extensively by many researchers [19–22]. Homogeneous transition-metal catalysts, such as Ru, Re, Co, and Ni complexes, have been used to reduce the CO₂ molecule by a multielectron reduction process [23–25]. CO₂ reduction by tricarbonyl rhenium(I) complex was first reported by Hawecker and coworkers [26], and the mechanism of such reactions have been studied previously [26–30]. The most efficient catalyst [Re(bpy)(CO)₃{P(OEt)₃}]⁺ was used for the selective photoreduction of CO₂ to CO



in a homogeneous system [27]. The drawback of using rhenium complex as a catalyst is that it reacts with CO_2 very slowly [28–32]. Binuclear rhenium(I) complexes with saturated bridging ligands have been synthesized for the photocatalytic CO_2 reduction [33]. Recently, the synthesis of dinuclear rhenium complexes of the 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) ligand and catalytic activity of tptz, as a bis(bidentate) ligand or as a bi- and tridentate chelating ligand, has been reported [34].

The reduction of CO_2 to CO using visible light can be used to cycle CO_2 gas [8, 17, 35–38]. Hawecker and coworkers used Re(I) pyridyl complex as a catalyst for CO_2 reduction into CO [26]. In addition, the same reaction has been carried out by using sacrificial amine as an electron source [27, 30]. Re(4,4-But₂bpy)(CO)₃Cl has been used as a catalyst for the same purpose at p-type silicon photocathodes when illuminated with visible light giving a photo-voltage of *ca* 600 mV. Thus, it makes the reduction of CO_2 possible at potentials of -1.2 V to -1.4 V versus saturated calomel electrode (SCE). A current efficiency of 97% was achieved under illumination. The duration of electrolysis was 3 h. However, attempts have been made to replace rhenium with more abundant metals for organometallic complexes due to the fact that rhenium is a rare metal found on earth [10, 39, 40].

Tetraphenylporphyrin iron chloride complex (Fe(TPP)Cl) was previously used for CO_2 reduction to CO and was claimed to be an efficient electrocatalyst for CO_2 reduction. 95% of current efficiency was reported and CO was reported to have high selectivity compared to H_2 at a mercury pool cathode when 2,2,2-trifluoroethanol ($\text{CF}_3\text{CH}_2\text{OH}$) was used as a proton source. Reduction of CO_2 to CO was carried out in a visible light at illuminated p-type Si photocathode using Fe(TPP)Cl in the presence of $\text{CF}_3\text{CH}_2\text{OH}$ as a proton source gave a current efficiency >90% and a high selectivity over H_2 formation. The potential of *ca* -1.2 V versus SCE was required under illumination. In the dark, on vitreous carbon, a potential of -1.85 V versus SCE was required. Iron(0)pentafluorotetraphenylporphyrin (Fe(PFTPP)Cl) was reported to be more positive potential than Fe(TPP)Cl, because the strong electron withdrawing fluorogroups shifted the potential for electrocatalysis about 400 mV positive compared to that of Fe(TPP)Cl [41].

The economic and efficient conversion of overabundant CO_2 into sources of fuel by means of renewable solar energy is one of the important objectives [42–45]. This work presents the electrochemical catalysis of CO_2 reduction into CO by cobalt(III)tetraphenylporphyrin [Co(TPP)Cl] at carbon and illuminated p-type Si electrodes.

2. Materials and Methods

Chemicals, solvents, Co(TPP)Cl, and $\text{CF}_3\text{CH}_2\text{OH}$ were purchased from Aldrich and used as received. Methyl cyanide (CH_3CN) was purified by distillation over calcium hydride. The single crystal B-doped p-type Si ($1\text{--}10\text{ cm}^{-1}$, (111) face, thickness $500\text{--}550\ \mu\text{m}$) was supplied by Silicon Materials (Germany). The ohmic contacts were made using Ga-In eutectic and silver epoxy resin by the method of Tamaki et al. [43]. The photoelectrochemical cell was described earlier [45].

Cyclic voltammetric experiments were carried out using an Autolab PGSTAT 30 potentiostat. A conventional three-electrode arrangement was employed, consisting of a vitreous carbon working electrode, a platinum wire as the auxiliary electrode, and Ag^+/AgCl as a reference electrode.

The electrolysis cells were degassed with argon gas to remove oxygen. The cell was filled with an electrolyte (a solvent containing $0.2\ \text{M}$ $[\text{Bu}_4\text{N}][\text{BF}_4]$). The volume of electrolyte was 14 mL, out of which 5 mL occupied the working electrode compartment. About 9–10 mL gas phase took place at the working electrode part. $0.35\ \text{mM}$ catalyst Co(TPP)Cl was added and dissolved in 5 mL dry CH_3CN and stirred under Ar in electrochemical cell which was under Ar. Cyclic voltammetric measurements of Co(TPP)Cl were carried out under Ar; then, the solution was bubbled with CO_2 (saturated with CO_2). The cyclic voltammetry of Co(TPP)Cl was done under CO_2 atmosphere to know the reduction catalytic CO_2 . $\text{CF}_3\text{CH}_2\text{OH}$ was added to improve both efficiency and catalyst life time, without any significant formation of H_2 .

The electrolysis was carried out at the fitting potential and the current was recorded during the course of electrolysis versus the time. In addition, the charge passed was recorded. The electrolysis was stopped when the current decayed after 1.4 h.

3. Results and Discussion

The electrocatalytic behavior of Co(TPP)Cl was tested by cyclic voltammetry in the absence of CO_2 .

Figure 1 shows the typical cyclic voltammetry of Co(TPP)Cl at carbon electrode in the absence of CO_2 . The cyclic voltammetry of the complex exhibits two successive reduction waves. The first wave is reversible corresponding to $\text{Co(II)}/\text{Co(I)}^-$ (one electron) at $E_{1/2} = -0.76$ V, and the second wave is irreversible corresponding to $\text{Co(I)}^-/\text{Co(0)}^{2-}$ (two electrons, one electron for second process of Co(TPP)Cl, $E_p = -1.98$ versus V, and maybe the farther electron related to reduction of complex); potentials cited are versus Ag/AgCl.

Figure 2 shows the different scan rate in $0.1\ \text{M}$ $[\text{Bu}_4\text{N}][\text{BF}_4]$ -95% MeCN+ 5% DMF at vitreous carbon

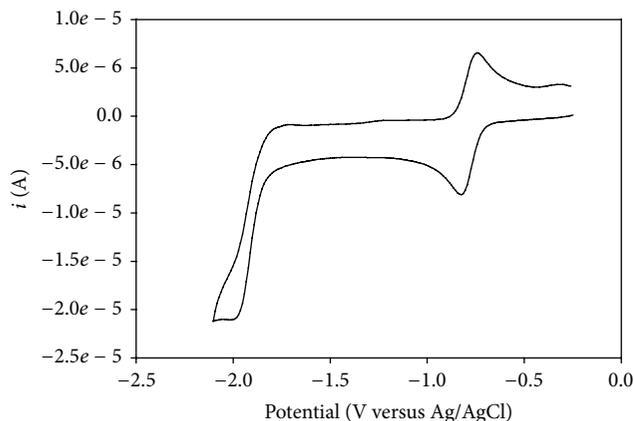


FIGURE 1: Cyclic voltammetry of 0.20 mM Co(TPP)Cl in 0.1 M $[\text{Bu}_4\text{N}][\text{BF}_4]$ -95% MeCN+ 5% DMF, scan rate 100 mVs^{-1} at vitreous carbon electrode under Ar.

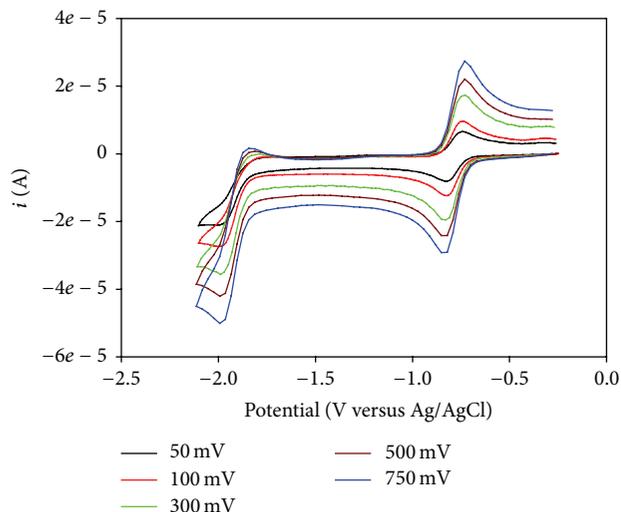


FIGURE 2: Cyclic voltammograms of 0.20 mM Co(TPP)Cl at carbon vitreous electrode, different scan rate in 0.1 M $[\text{Bu}_4\text{N}][\text{BF}_4]$ -95% MeCN+ 5% DMF.

and Figure 3 shows the plots of i_p^{red} versus $n^{1/2}$ of the first and second processes of Co(TPP)Cl, which are diffusion-controlled and involve an electrochemically reversible one-electron transfer. The plot of peak current i_p^{red} versus $n^{1/2}$ is linear which means no complicated mass transfer control of one electron-transfer rate. The diffusion of first wave is calculated according to the following:

$$i = 7.4 \times 10^{-6} \text{ A}$$

$$I = 1.04 \times 10^{-4} \text{ A} \cdot \text{cm}^{-2} \quad (1)$$

Area of electrode is 0.071 cm^2

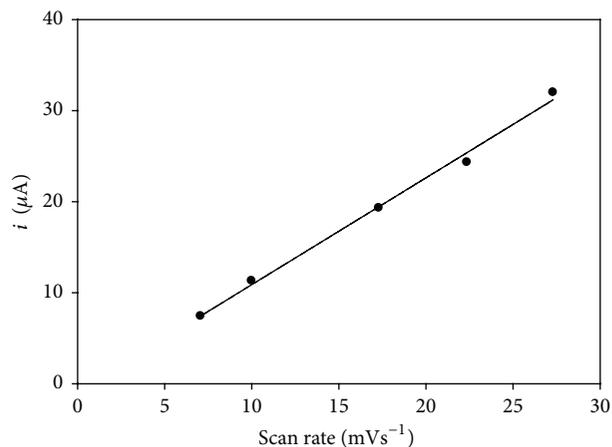


FIGURE 3: The plots of i_p^{red} versus $n^{1/2}$, $\text{Co(I)}^{-1}/\text{Co(0)}^{-2}$ reduction wave.

$$I_p = -\left(2.69 \times 10^5\right) n^{3/2} D^{1/2} \nu^{1/2} \quad (2)$$

Randles-Sevcik Equation

$$D = 1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}. \quad (3)$$

3.1. Electrocatalytic Reduction of CO_2 by Co(TPP)Cl on Vitreous Carbon and p-Type Si Electrodes. Figure 4(a) shows the electrocatalytic reduction of CO_2 by Co(TPP)Cl on vitreous carbon, under argon. The current density of second reduction of Co(TPP)Cl is around $2.24 \times 10^{-4} \text{ A} \cdot \text{cm}^{-2}$. In the same figure, the cyclic voltammetry of the catalyst shows that CO_2 interacts with the reduced catalyst. The second wave process increased in height and became irreversible under CO_2 , and the catalytic current density increased to $1.76 \times 10^{-3} \text{ A} \cdot \text{cm}^{-2}$.

As known, the direct reduction of CO_2 at vitreous carbon electrode is around -2.2 V versus Ag/AgCl. In the presence of Co(TPP)Cl, the carbon CO_2 shifted to -1.85 V which is more positive in comparison with the direct reduction. At p-type Si electrode, the second wave reduction of Co(TPP)Cl shifted to a more positive value *ca* 300 mV under illumination of light (Figure 4(b) in the absence and presence of CO_2).

Figure 5 shows the comparison of cyclic voltammetry of Co(TPP)Cl at p-type Si electrode in dark and light which proves the shifting of potential in the presence of light around 300 mV.

3.2. Preparative-Scale Electrolysis. Preparative bulk photoelectrosynthesis of CO on the p-type Si photocathode was performed in 1 M $[\text{Bu}_4\text{N}][\text{BF}_4]$ -95% MeCN+ 5% DMF at room temperature in an H-type in the presence of 0.2 mM Co(TPP)Cl and 0.28 mM $\text{CF}_3\text{CH}_2\text{OH}$. The gas chromatography (GC-TCD) confirmed the formation of CO with a current efficiency of *ca* 65%. During the course of 1.4 h (-1.55 V versus Ag/AgCl), the charge passed was 4.18 C, the yield of CO was 14 μmoles , and *ca* 10% amount of hydrogen was produced as a by-product (Figure 6).

In a separate experiment at the same conditions, the bulk electrolysis at carbon electrode was carried out at -1.85 V

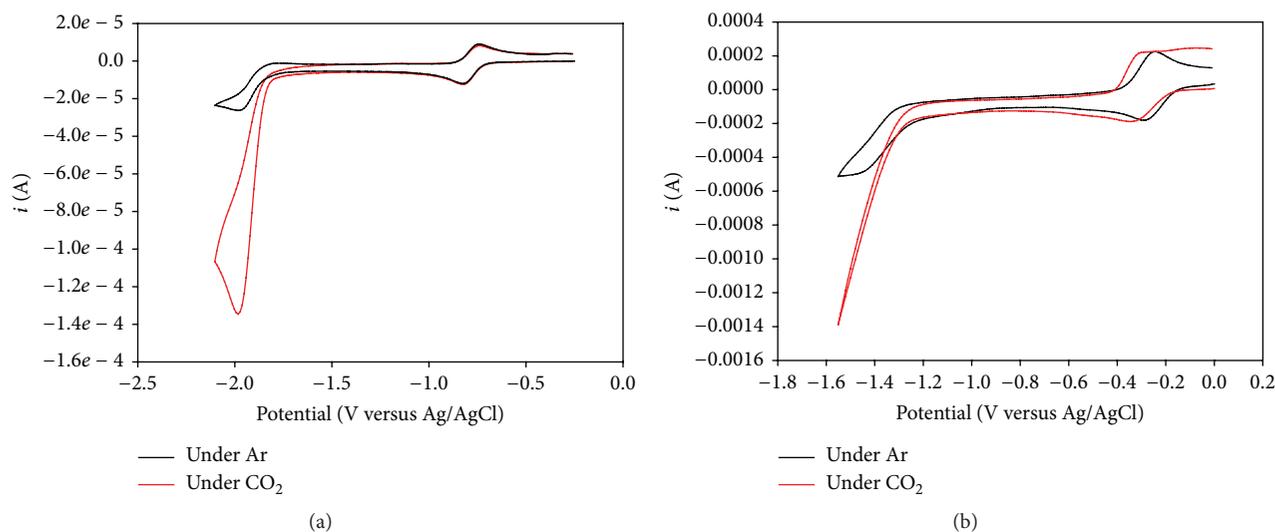


FIGURE 4: Cyclic voltammetry of 0.20 mM Co(TPP)Cl in 0.1 M $[\text{Bu}_4\text{N}][\text{BF}_4]$ -95% MeCN+ 5% DMF, scan rate 100 mVs^{-1} (a) at a vitreous carbon electrode and (b) at illuminated $1\text{--}10 \text{ ohm cm}^{-1}$ p-type Si electrode.

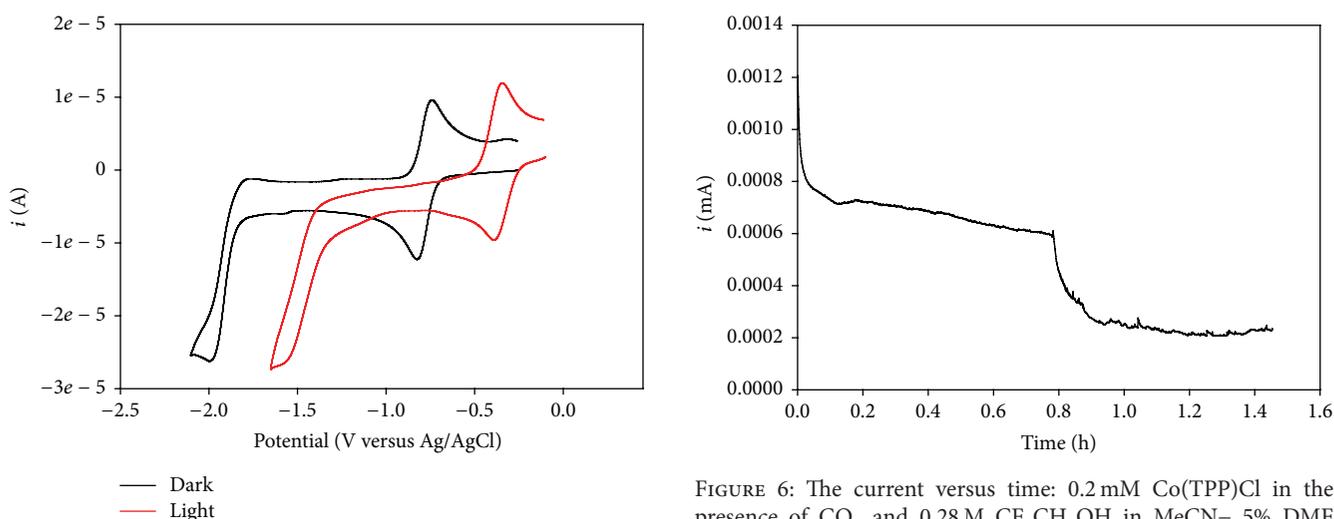


FIGURE 5: Cyclic voltammetry of 0.20 mM Co(TPP)Cl in 0.1 M $[\text{Bu}_4\text{N}][\text{BF}_4]$ -95% MeCN+ 5% DMF, scan rate 100 mVs^{-1} at p-type Si electrode in dark and at illuminated p-type Si electrode under Ar.

versus Ag/AgCl. CO_2 was converted into CO with a current efficiency of *ca* 71.6%, where the yield of CO was $19 \mu\text{moles}$ and the charge passed was 5.3 C. Also, a small amount of hydrogen was obtained which can be ignored. The current efficiency to produce CO at both carbon and p-type Si electrodes is smaller but the amount of hydrogen is different which may be because of coupling of homogeneous catalysts for the reduction of CO_2 with heterogeneity of small amount of H_2O . Reduction of CO_2 by photocathode at p-type Si electrode is shown in Figure 7 and the course of electrolysis was 1.4 h.

FIGURE 6: The current versus time: 0.2 mM Co(TPP)Cl in the presence of CO_2 and 0.28 M $\text{CF}_3\text{CH}_2\text{OH}$ in MeCN- 5% DMF containing 0.1 M $[\text{Bu}_4\text{N}][\text{BF}_4]$, at p-type Si electrode.

Table 1 summarises the results of both electrocatalysis and photoelectrocatalysis of CO_2 reduction by Co(TPP)Cl at carbon and p-type Si electrodes.

4. Conclusion

It has been shown that the CO_2 reduction can be achieved by using a simple cobalt porphyrin complex as a catalyst in the electroreduction that is carried out in dark (carbon electrode) and under illumination (p-type Si electrode). At carbon electrode, cobalt porphyrin catalyzes conversion of CO_2 to CO with the current efficiency of 72%. On the other hand, the current efficiency of CO_2 to CO reduction was only 65% at p-type Si electrode in the presence of cobalt porphyrin. However, $\text{CF}_3\text{CH}_2\text{OH}$ was added to improve the catalysis of CO_2 reduction.

TABLE 1: Current efficiencies and turnover numbers of electrocatalytic reduction of CO₂ catalyzed by Co(TPP)Cl at both carbon and p-type Si electrodes. T.N. = moles of product/moles of catalyst.

Electrode	CPE potential (SCE)	Number of moles of catalyst μ mole	Time of experiment/h	Charge coulomb/C	Current efficiency* CO	T.N. CO	Number of CO μ moles	Current efficiency H ₂
Carbon	-1.85	1	1.4	5.4	72	19	19	1.2
p-type Si	-1.55	1	1.4	4.2	65	13.9	13.9	10

*The rest of current efficiency was unknown which might have been consumed by conversion of CO₂ into oxalate or formate. Saveant and coworker reported that CO₂ will be converted to oxalate or formate in the presence of a weak acid [42], or by decomposition of catalyst.

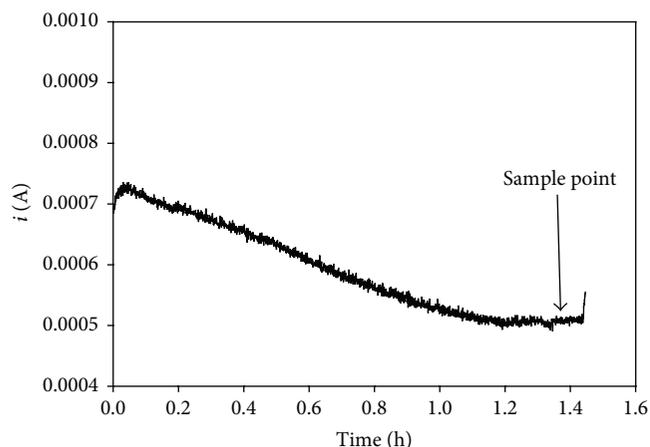


FIGURE 7: The current versus time: 0.2 mM Co(TPP)Cl in the presence of CO₂ and 0.28 M CF₃CH₂OH in MeCN- 5% DMF containing 0.1 M [Bu₄N][BF₄], at carbon electrode.

Under illumination at p-type Si electrode (boron-doped p-type H-terminated silicon), and in presence of cobalt porphyrin, the reduction of CO₂ to CO can be achieved at a potential *ca* 300 mV positive to that of an inert vitreous carbon electrode. The reduction of CO₂ to CO catalyzed by cobalt porphyrin was carried out at 1.85 V, but at p-type Si electrode it shifts more positive at -1.55 V versus Ag/AgCl.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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