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Solar Light-Driven Reduction of CO_2 on p-type Silicon Semiconducting Electrodes by Iron(0)pentaflourotetraphenylporphyrin

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Iron(0)pentaflourotetraphenylporphyrin [FeCl(PFTPP)] electrocatalyse the selective photoreduction of CO_2 to CO at illuminated p-type silicon photocathode at a potential 600 mV positive of that required for carbon and Hg electrodes with current efficiency of 22 % and the amount of hydrogen 35 %. Coupling of homogeneous Fe-porphyrins catalyse the reduction of CO_2 with heterogeneous H_2O reduction by photocathode p-type Si electrode. More H_2 production detected at a lower concentration of catalyst, whereas electrolysis on Hg and carbon electrode under the same condition as p-type Si showed very low H_2 production.

Keywords: CO_2 reduction, iron, photoelectrocatalysis, porphyrins, p-type silicon

1. INTRODUCTION

Carbon dioxide (CO_2) is a significant greenhouse gas, but at the same time it is a readily available source of carbon for the synthesis of new molecules. Electrocatalytic reduction of CO_2 is therefore extremely attractive process. Coupling of this reduction to solar light harvesting at semiconductor electrodes offers the potential to capture both energy and carbon in a single process. However, CO_2 is chemically inert and activation of the substrate therefore presents a key challenge [1].

The reduction of CO_2 to carbon monoxide (CO) using visible light affords a solar fuel [2-4], which provides a pathway for cycling a greenhouse gas [5-14]. Early work by Lehn, Geiger and their co-workers [15, 16] has reported the catalysis of electrochemical reduction of CO_2 by using Re(I) pyridyl complexes. This type of system has also been used to photocatalyse the reduction of CO_2 to CO in the presence of a sacrificial amine as an electron source [17, 18]. More recently, Kubiak and co-workers [19,20] have shown that Re(4,4-But_2bpy)$(CO)_3$Cl catalyses reduction of CO_2 to CO at p-type silicon photocathodes when illuminated with visible light. A photo-voltage of ca. 600 mV was achieved, facilitating the reduction of CO_2 at potentials of -1.2 V to -1.4 V versus saturated calomel (SCE). The system reduces CO_2 into CO under illumination, with a current efficiency of 97% during 3 hours of electrolysis. However, due no doubt to its scarcity on earth, research attempts have been made to replace rhenium with somewhat more abundant metals for organometallic complexes. The simple iron porphyrin, FeCl(tetraphenylporphyrin), [Fe(TPP)Cl], was reported to be an efficient and reasonably stable electrocatalyst for CO_2 reduction. Thus at a mercury pool cathode in the presence of 2,2,2-trifluoroethanol (CF_3CH_2OH) as a proton source, CO_2 to CO reduction occurs with a current efficiency of 95%, and high selectivity over H_2 formation. Reduction of CO_2 to CO can also be driven at a visible light illuminated p-type Si photocathode using Fe(TPP)Cl in the presence of CF_3CH_2OH as a proton source and CO is produced with a current efficiency >90 % and a high selectivity over H_2 formation. The systems operate at a potential of *ca* -1.2 V *versus* SCE while in the dark on vitreous carbon at a potential of -1.85 V *versus* SCE. One of many contemporary and important energy objectives is the economic and efficient conversion of over abundant CO_2 into sources of fuel by means of renewable solar energy. The scope of this work is the electrochemical catalysis of CO_2 reduction into CO by classical metal porphyrins at carbon and illuminated p-type Si electrodes.

We now show that FeCl(pentaflourotetraphenylporphyrin), Fe(PFTPP)Cl, can be used for CO_2 reduction to CO. Fe(PFTPP)Cl is more positive potential than Fe(TPP)Cl, because it possesses five strongly electron withdrawing pentafluorophenyl groups which decrease the electron density at the metal centre. In addition, the strongly withdrawing fluoro-groups shift the potential for electrocatalysis about 400 mV positive of that for Fe(TPP)Cl.

2. EXPERIMENTAL

Chemical and solvents such as porphyrins, Fe(TPP)Cl and Fe(PFTPP)Cl and CF_3CH_2OH were from commercial origin (Aldrich). CO_2 gas 99.9 % obtained from BOC. DMF and MeCN were purified by distillation over CaH. Bu_4NBF_4 was used as supporting electrolyte.

Electrochemical measurements were made with Autolab model 100 potentiostat. Electrochemical H type cell with three compartments was used with a vitreous carbon (0.07 cm^2) and Hg pool (2.5 cm^2) as working electrodes in cyclic voltammetry and controlled potential electrolysis, respectively. Platinum foil (2 cm^2) as counter electrode and potentials are referred to aqueous LiCl SCE in DMF or MeCN-DMF solution. The single crystal B-doped p-type Si (1-10 and 40-100 Ω cm^{-1}, (111) face, thickness 500-550 μm) was supplied by Silicon Materials. It was converted to the H-terminated form by HF etching. The ohmic contacts were made using Ga-In eutectic and silver epoxy resin by the method of Wrighton et al. [21] The photoelectrochemmical cell was described earlier [22-24]. Gas chromatography was carried out using a Perkin-Elmer Clarius 500 instrument fitted with a 5 Å molecular sieve column (800/100 mesh, 6’ × 1/8”) and thermal conductivity detector.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry of Fe(PFTPP)Cl

Evidence for the electrocatalytic behaviour of Fe(PFTPP)Cl was examined by cyclic voltammetry and controlled potential electrolysis experiments in absence and presence of CO_2. Cyclic voltammetry of iron(III) porphyrin complex under Ar on both illuminated p-type silicon and vitreous carbon electrodes shown in Figure 1 (a and b). On a vitreous carbon electrode three successive reduction processes were observed in 0.1 M tetrabutylammonium tetrafluoroborate (NBu_4BF_4)-dimethylformamide (DMF) at potentials $E_{1/2}$ = -0.14, -0.72, and -1.2 V (*versus* SCE) corresponds to Fe(III)/Fe(II), Fe(II)/Fe(I) and Fe(I)/Fe(0) processes respectively (Figure 1a). The response on illuminated p-type Si is dramatically different from that in the dark, at illuminated p-type Si electrode the potentials of these processes shift more than ca. 500 mV positive of that observed at vitreous carbon electrode (Figure 1b). Similar behavior was reported by Bard and coworkers, nearly forty years ago, that the dark reduction of the $[Ru(bpy)_3]^{2+/1+}$ system on p-type Si in MeCN and noted the shift in redox response to more positive values upon illumination, the magnitude of the shift in the redox couples was of a similar magnitude, 540 – 600mV [25].

The peak current of Fe (I)/Fe(0) process at p-type Si electrode increases towards two electron, perhaps due to either adsorption of the catalyst on the H-Si surface or heterogeneous catalysis reduction of trace amount of water present in solvent at the surface of p-type Si which may influence the chemistry on p-type Si more than on vitreous carbon.

The cyclic voltammetry of the catalyst shows that CO_2 does interact with the reduced catalyst, as noticed by the fact that Fe(I)/Fe(0) process increases in height and become irreversible under CO_2. However, the peak current and the turnover numbers are very small. Addition of weak acid, such as trifluoroethanol, results in dramatic improvement of catalytic efficiency and life time of the catalyst at both carbon and p-type Si electrode (Figures 2 and 3). This catalytic improvement is due to the stabilisation of an iron-CO_2 adduct ($Fe^{II}CO_2^{2-}$ complex) by hydrogen bonding as described in the mechanism outlined by Saveant and co-workers [26-27].

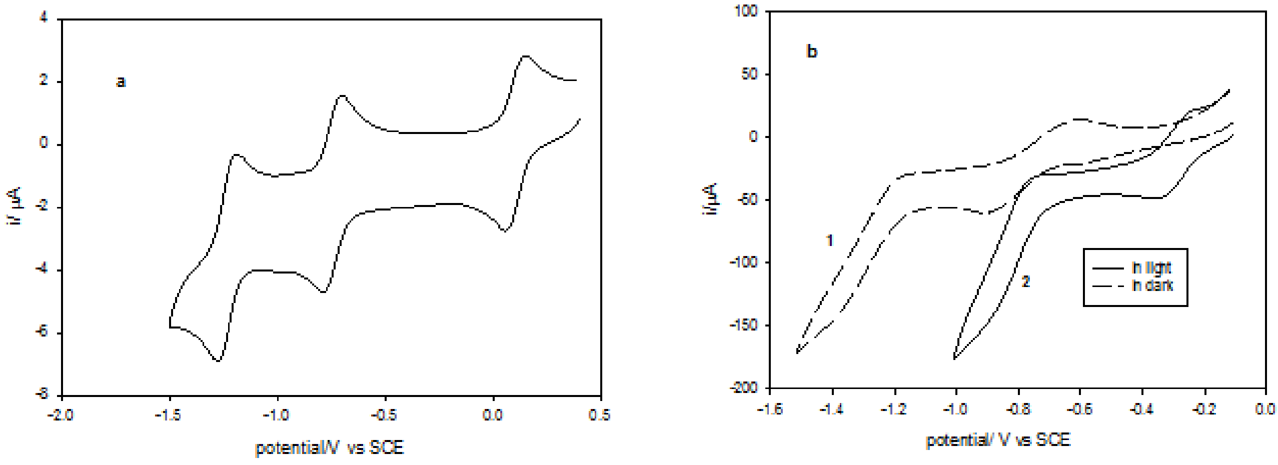

Figure 1. Cyclic voltammograms of Fe(PFTPP)Cl in a solvent mixture (MeCN-5 % DMF) containing 0.1 M NBu_4BF_4 at a scan rate of 100 $mV\cdot s^{-1}$. (a) At a vitreous carbon electrode. (b) At an illuminated p-type H-Si electrode (1) in the dark, (2) illuminated under a Krüss halogen fibre optic lamp ($90mW\cdot cm^2$, λ_{max} =650nm).

Figure 1 shows the cyclic voltammetry of Fe(PFTPP)Cl in (MeCN-5 % DMF v/v-0.1 M NBu_4BF_4) at carbon and p-type Si electrode in the dark (B-doped, Si-H surface termination, 1- 10Ω cm^{-1}) and when illuminated (b), using a Krüss halogen fibre optic lamp (90 mW/cm^2, λ_{max} = 650 nm) at the same electrode. The solvents are mixed by this ratio because the stability of the insulating epoxy resin protecting the copper wire/silver epoxide/gallium contact on the p-type Si, which limited the choice of solvent. The mixed solvent MeCN-5 % DMF (v/v) was a compromise between the poor solubility of the complexes in 100 % MeCN and the deterioration of the epoxy resin in 100 % DMF. However, there is a significant shift of the sequential reduction process upon illumination corresponding to a photovoltage of >470 mV. The potential range is confined to that covering the reduction of the Fe(II)/Fe(I) and Fe(I)/Fe(0) couples because the H-terminated p-type Si is oxidised at potentials positive of about -0.2V *versus* SCE and becomes inactivated [28]. Whereas the Fe(II)/Fe(I) couple shows a reasonable well-defined behaviour and parallels that on vitreous carbon, the Fe(I)/Fe(0) process observed on vitreous carbon becomes irreversible on the p-type Si surface. The structure of the inner reaction layer at the semiconductor may promote halide loss and further electron-transfer to the porphyrin ring.

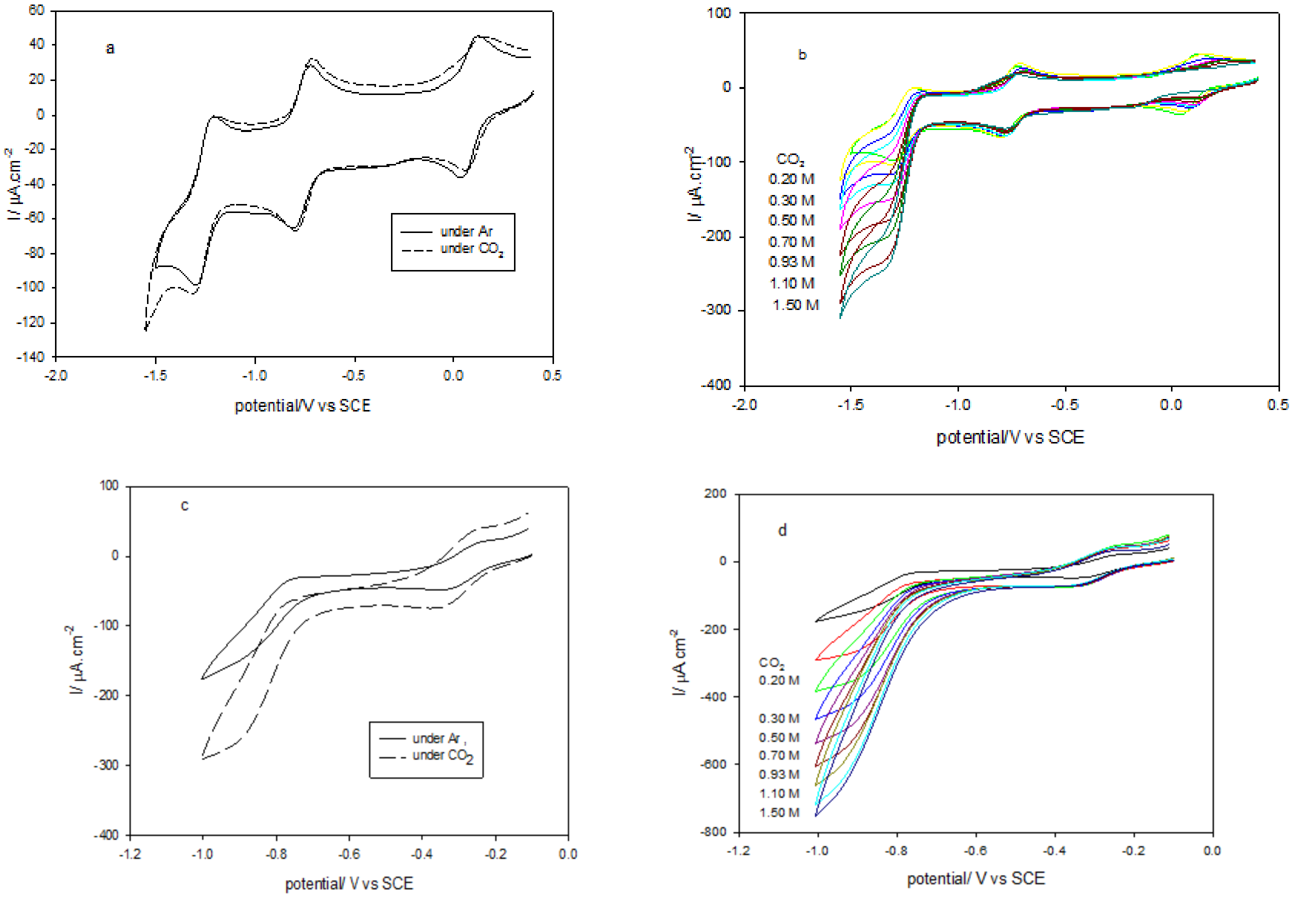

Figure 2. Cyclic voltammograms of Fe(PFTPP)Cl in a solvent mixture (MeCN-5 % DMF) containing 0.1 M NBu_4BF_4 at a scan rate of 100 $mV{\cdot}s^{-1}$. (a) At a vitreous carbon electrode under Ar and when saturated with CO_2 (a) and at various concentrations of CF_3CH_2OH in the presence of CO_2 *ca* 0.25M (c); At an illuminated p-type H-Si electrode (b) and at various concentrations of CF_3CH_2OH in the presence of saturated CO_2 (*ca* 0.25M) (d).

Figure 2 shows the cyclic voltammetry of Fe(PFTPP)Cl at a conventional vitreous carbon electrode under argon and when saturated with CO_2 *ca* 0.25 M (a), also in the presence of CF_3CH_2OH at various concentrations of the proton source in the same electrolyte (b)**,** at illuminated p-type Si under the same conditions (c and d). Electrocatalysis at the inert vitreous carbon electrode is paralleled by photoelectrocatalysis at the p-type Si electrode although at the higher acid concentrations the limiting current densities are higher at the illuminated semiconductor. The increase of current density at p-type Si electrode may be due to the two products, CO and H_2, while at vitreous carbon electrode the dominant product is CO. The current density increases with increasing [CF_3CH_2OH] up to about 1.5 M, after which the electrocatalysis becomes independent of the acid concentration, indicating protonation is no longer rate-limiting.

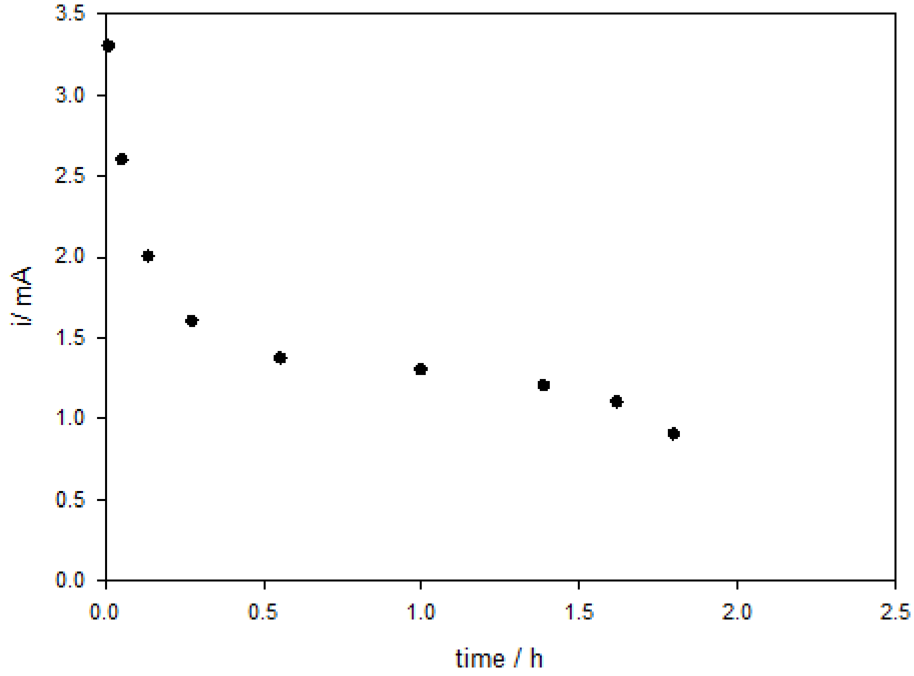

Figure 3. The current *versus* time: 0.11 mM Fe(PFTPP)Cl in the presence of CO_2 and 1.5 M CF_3CH_2OH in MeCN-5 % DMF containing 0.1 M NBu_4BF_4, at mercury pool cathode.

Table 1 represent the comparison of the reduction potentials (V *versus* SCE) in MeCN-5% DMF (v/v) containing 0.1 M NBu_4BF_4 for both Fe(TPP)Cl and Fe(PFTPP)Cl at vitreous carbon and p-type Si electrodes. Data shows that the reduction potentials $E_{1/2}$ quoted *versus* SCE and were determined at 100 mVs^{-1}. The overall trend in reduction potentials is as expected. The complex Fe(PFTPP)Cl which possesses a total of 20 electron-withdrawing fluoro-substituents on the phenyl groups is easier to reduce across all the Fe(III)/Fe(II), Fe(II)/Fe(I) and Fe(I)/Fe(0) redox levels than is its Fe(TPP)Cl counterpart. Thus the $Fe(PFTPP)Cl^{0/1-/2-/3-}$ couples occur at potentials which are successively 330, 350 and 400 mV positive of those for the corresponding $Fe(TPP)Cl^{0/1-/2-/3-}$ couples at vitreous carbon electrode. The difference of shifting at p-type Si electrode may be related to the effect of light intensity on the voltammetric response.

Table 1. The comparison of reduction potentials (V *versus* SCE) in MeCN-5 % DMF (v/v) containing 0.1 M NBu_4BF_4 at carbon and p-type Si electrodes for Fe(TPP)Cl and Fe(PFTPP)Cl complexes.

Complex	Vitreous carbon electrode			P-type Si electrode		
	$^1E_{1/2}$	$^2E_{1/2}$	$^3E_{1/2}$	$^1E_{1/2}{}^*$	$^2E_{1/2}$	^3E_p
Fe(PFTPP)Cl	0.14	-0.72	-1.30	-	-0.28	-0.83
Fe(TPP)Cl [22]	-0.19	-1.07	-1.60	-	-0.45	-1.1

* p-type Si is oxidised at potentials positive of about -0.2V *versus* SCE and becomes inactivated

3.2. Electrosynthesis of CO catalysed by Fe(PFTPP)Cl at both vitreous carbon and p-type Si electrodes

The electrolysis of a saturated CO_2 solution {mercury pool, -1.4 V *versus* SCE; MeCN-5 % DMF (v/v); 0.1 M NBu_4BF_4; 1.5 mM CF3CH2OH} in the presence of 0.11 mM Fe(PFTPP)Cl as the electrocatalyst gave 21 µmoles of CO after the passage of 90.5 µmoles of electrons (8.73 C) during the course of 1.8 h with a current efficiency of *ca* 46 % after 38 turnovers. A small amount of hydrogen is formed with a current efficiency of 1.1%. In a separate experiment, when the concentration of Fe(PFTPP)Cl was increased to 0.2 mM, there was a small increase in the current efficiency to 53 % (36 µmoles CO; charged passed 12.3 C). This system is less efficient at producing CO as compared to Fe(TPP)Cl , but in addition to CO, it may produce some other products, possibly oxalate and formate [22], which have not been analyzed in this study.

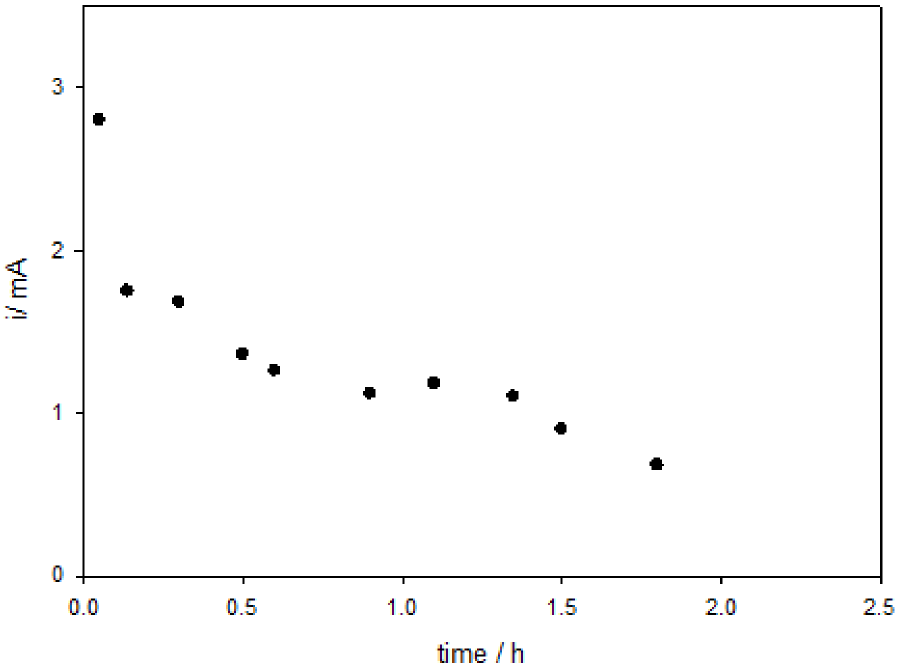

Figure 4. The current *versus* time: 0.11 mM Fe(PFTPP)Cl in the presence of CO_2 and 1.5 M CF_3CH_2OH in MeCN-5 % DMF containing 0.1 M NBu_4BF_4, at p-type Si electrode.

Under the similar conditions, bulk photoelectrosynthesis of CO in the presence of Fe(PFTPP)Cl on the p-type Si photocathode together with examination of the gas phase by gas chromatography established the formation of CO. Production of CO occurred with a current efficiency of 22 % after 11 turnovers during the course of 1.8 h. The photoelectrolysis was carried out at -0.90 V *versus* SCE. The charge passed was 5.4 C, 6 µmoles CO, 0.11 mM Fe(PFTPP)Cl, 1.5 M CF_3CH_2OH, also an amount of H_2 was co- produced with current efficiency 38.5 % after 19.6 turnovers and 10.8 µmoles of H_2. Possibly oxalate or formate may be responsible for the rest of current which was more than 43% but these have not been determined. A plot of current *versus* charge-passed is shown in Figure 4.

CO and H_2 were analysed by gas chromatography with thermal conductivity detector (GC-TCD). Table 2 summarises the results for the Fe(PFTPP)Cl in terms of charge passed at both vitreous carbon electrode and an illuminated p-type H-Si electrode, CO and H_2 yields, current efficiency and number of turnovers (T.N).

Table 2. Comparing current efficiencies and turnover numbers of electrocatalytic reduction of CO_2 catalysed by Fe(PFTPP)Cl at p-type Si and carbon electrode.

Electrode	Potential (SCE)	Number of moles of catalyst /µmole	Time of experiment/h	Charge coulomb/C	Current efficiency CO	T.N CO	µmol of CO	Current efficiency H_2	T.N H_2
Vitreous carbon electrode	-1.40	0.55	1.8	8.37	46	38.2	21	1.1	2
P-type Si electrode	-0.90	0.55	2.2	5.4	22	10.9	6	38.5	19.6

T.N.= moles of product/moles of catalyst

3.3. Calculation of k_{cat} at carbon electrode and p-type Si electrode

Figure 5 shows comparative data for the ratio i_{cat} / i_o at the vitreous carbon electrode and the illuminated p-type Si electrode, *versus* [CF_3CH_2OH] under CO_2 in the presence of Fe(PFTPP)Cl. The peak catalytic current, i_{cat}, is measured at 100 mVs^{-1} and i_o is the peak current measured for the primary one-electron reduction step at the same scan-rate. From this figure, it is apparent that at both vitreous carbon and p-type Si electrodes the values of i_{cat} / i_o become independent of the acid concentration at *ca* 0.75 M in the MeCN-5 % DMF. We should note that Fe(PFTPP)Cl is not adsorbed on the silicon surface. However, removal of the electrode after cycling in the presence of the complex at potential between -0.20 and -1.2 V versus SCE, washing with electrolyte and transferring to fresh electrolyte solution gave a current response indicative of the formation of a catalytic film on the electrode surface. The response for the system at vitreous carbon is similar to that at the illuminated p-type Si.

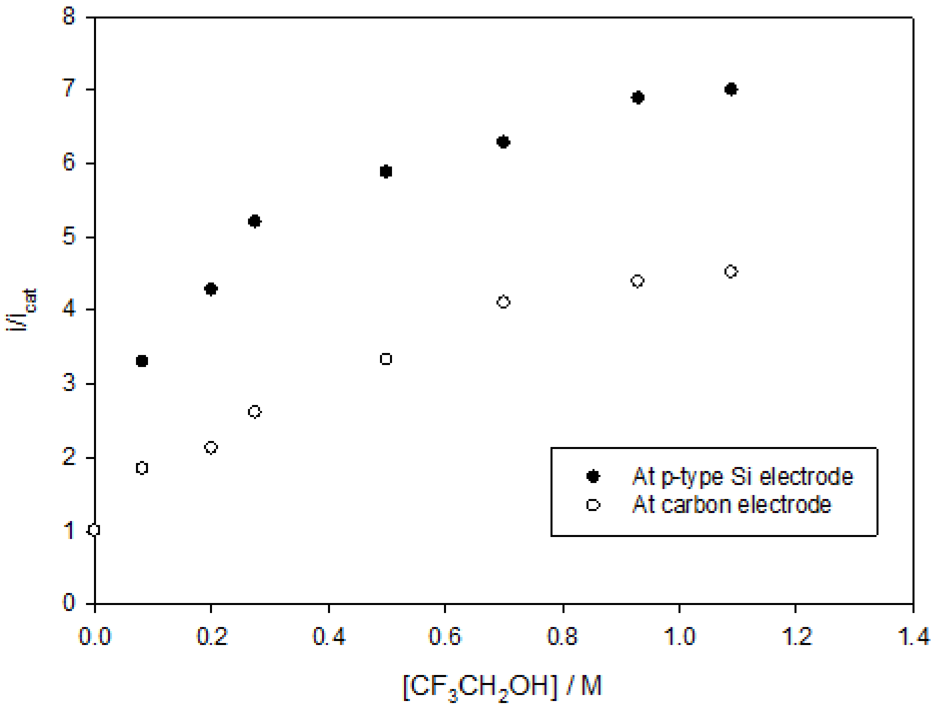

Figure 5. Effect of the acid concentration on i_{cat}/i_0 ratio at a vitreous carbon electrode and an illuminated p-type H-Si electrode.

In the acid-independent regimes, the magnitude of i_{cat} / i_o for the electrocatalysis on the illuminated p-type Si is about twice that observed on vitreous carbon which is expected because at p-type Si there is two products 22 % CO and 38.5 % H_2 while on the product 46 % CO with 1.1 % H_2. Following the approach of Dubois and others [23, 24, 29], the rate constant $k^{Si}{}_{obs}$ at both vitreous carbon and illuminated silicon electrodes can be estimated from the i_{cat}/i_0 data using the relationship shown in Equation (1), where F, R and T are the Faraday constant, the gas constant and temperature, respectively; n is the number of electrons involved in the turnover.

$k^{Si}{}_{obs}=0.1992(F\nu/RTn^2)(i_{cat}/i_0)^2$ Equation 1

In the acid independent regime, the rate constant ($k^{Si}{}_{cat}$, 23 °C) for the catalysis at illuminated p-type Si is calculated to be (0.36 ± 0.1) x 10^2 $M^{-1}s^{-1}$ [5], whereas the corresponding rate constant at vitreous carbon ($k^{C}{}_{cat,}$) is estimated to be (0.13 ± 0.1) x 10^2 $M^{-1}s^{-1}$, taking the saturated concentration of CO_2 in MeCN to be 0.25 M at 23 °C for both systems.

3.4. Co-generation of CO and H_2 by variation of Fe-porpyrin catalyst concentration

Coupling of homogeneous Fe-porphyrins catalyse the reduction of CO_2 with heterogeneous H_2O reduction by photocathode p-type Si electrode, as recently described by Kubiak for the Re photoelectrocatalysis [14].

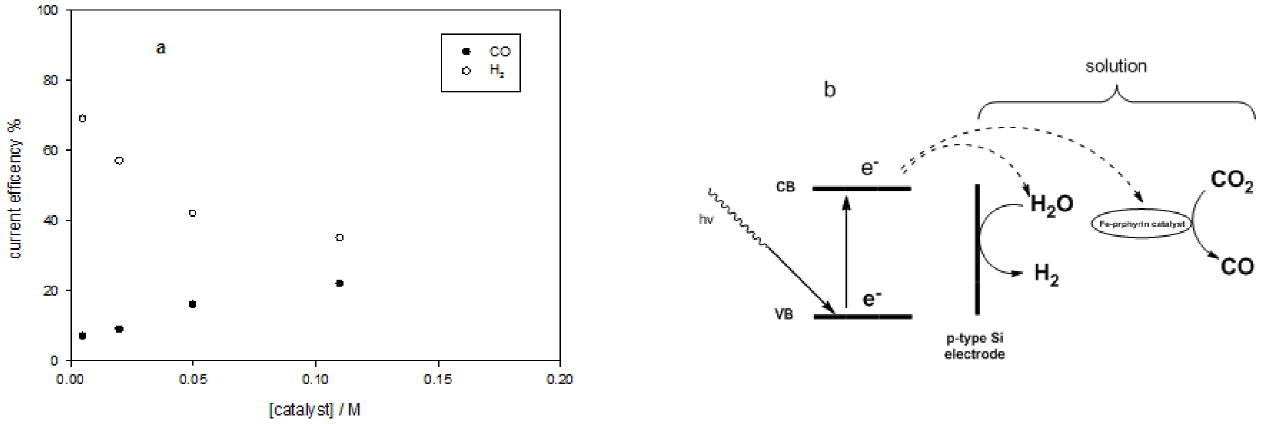

Figure 6. (a) Current efficiency of CO and H_2 formation for different concentrations of catalyst, (b) Heterogeneous catalytic role of p-type Si for H_2 reduction from H_2O and the Fe-porphyrin role as CO_2 reduction catalysts [14].

In a Fe-porphyrin system, it is notable that increasing of porphyrin concentration led to an increase in CO yield and a decrease in H_2 yield (Figure 6), whereas (dark) electrolysis on Hg or vitreous carbon electrodes under the same conditions as illuminated p-type Si showed very low H_2 production (less than 5%). For example, photoelectrolysis of a 0.05 mM solution of Fe(PFTPP)Cl in the presence of 1.5 M of CF_3CH_2OH reducing the current efficiency of CO formation to 16 % whilst increasing that of hydrogen formation to 42 % during the course of 1.8 h. Figure 6b shows a schematic for the two pathways on p-type Si which is qualitatively explained by the heterogenous reduction of protons at the semiconductor surface and homogenous reduction of CO_2 by the molecular catalyst. This suggests that electrode material and Fe-porphyrin concentration play an important role in determining selectivity of products.

4. CONCLUSIONS

Simple iron(0) pentaflurotetraphenylporphrin electrocatalyst [Fe(PFTPP)Cl] can enable light assisted reduction of CO_2 to CO at boron-doped p-type H-terminated silicon photocathodes at a potential *ca* 550 mV positive of that at an inert vitreous carbon electrode. The Fe(PFTPP)Cl is reduced at both vitreous carbon and p-tpe Si electrode more positive than its analogue Fe(TPP)Cl because Fe(PFTPP)Cl has the strongly withdrawing fluoro-groups which shift the potential for electrocatalysis about 400 mV positive of that for Fe(TPP)Cl.

The electrocatalytic reduction of CO_2 to CO at a vitreous carbon electrode in the presence of Fe(PFTPP)Cl in MeCN-5 % DMF (v/v), 0.1 M NBu_4BF_4; and 1.5 mM CF_3CH_2OH at 23 °C was carried out at -1.4 V with current efficiency 46 % and small amount of H_2 (less than 5 %) while on an illuminated p-type H-Si electrode was performed at -0.9 V with 22 % CO and significant H_2 product ca 38.8 during 1.8 h.

We can conclude here that the photoreduction of CO_2 to CO on p-type Si photocathode is possible with Fe-porphyrin catalysis in very high current efficiency and turnover numbers. In this system, the reduction of CO_2 at illuminated p-type Si is achieved at potential up to 600 mV less than required at Hg electrode. Fe-porphyrin catalysis of CO_2 reduction occurs at potential positive of the recently reported [30] Re system and employ abundant metal, Fe vs Re.

In saturating proton flux conditions, kcat under the visible light (90 $mWcm^{-2}$, λ_{max} = 650 nm) is two-fold higher than that under the dark. We tentatively suggest that the smaller turnover frequency observed for the photoelectrocatalysis by Fe(PFTPP)Cl ($k^{Si}{}_{cat} = (0.36 \pm 0.1) \times 10^2\ M^{-1}s^{-1}$) as compared with that at vitreous carbon in the dark ($k^{c}{}_{cat} = (0.13 \pm 0.1) \times 10^2\ M^{-1}s^{-1}$) is also a consequence of the different nature of the interfacial regimes of the two materials.

Coupling of homogeneous Fe-porphyrins catalyse the reduction of CO_2 with heterogeneous H_2O reduction or proton reduction by photocathode p-type Si electrode. This observation is similar to the work recently described by Kubiak [14] for the Re photoelectrocatalysis. More H_2 production detected at a lower concentration of the catalyst Fe(PFTPP)Cl at p-type Si than at higher concentrations, whereas (dark) electrolysis on Hg under the same conditions as illuminated p-type Si showed very low H_2 production.

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