Int. J. Electrochem. Sci., 17 **(2022)** Article Number: 220147, doi: 10.20964/2022.01.46

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Metalloporphyrin Catalysed Photoelectrochemical Reduction of CO_2 at p-type Silicon Semiconducting Electrode

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Received: 7 October 2021 / *Accepted:* 19 November 2021 / *Published:* 6 December 2021

In the present study, the photoelectrocatalytic performance of a homogenous manganese(III) teraphenyl porphyrin (Mn(TPP)Cl) complex for carbon dioxide (CO_2) to carbon monoxide (CO) reduction has been evaluated. The electrocatalysis experiment was carried out at a Group IV (boron-doped p-type H-terminated silicon) semiconducting electrode in 0.1 M $[NBu_4][BF_4]$–MeCN) electrolyte. The study was carried out at different concentration of the catalyst (0.05, 0.5 and 1 mM) and Brönsted acid (CF_3CH_2OH, 4-32 mM) under dark and illuminated (with polychromatic light) conditions. Results of the study indicated that the CO_2 reduction takes place at a much lower potential with appreciable current efficiency (48.2%) under illuminated conditions as compared to the dark condition. Besides, as compared to the previously studied carbon electrode system, the results are much better. Other than CO, molecular hydrogen generated as the second main product with current efficiency 42%.

Keywords: Carbon dioxide; Electrochemical reduction; Photoelectrocatalytic; Metalloporphyrin.

1. INTRODUCTION

Carbon dioxide (CO_2) is a linear triatomic molecule with immense importance in the nature. For instance, it is a primary greenhouse gas that keeps the earth's temperature balanced and used in photo-synthesis process.[1] However, an increased CO_2 concentration (due to anthropogenic emission) is equally responsible for the global warming and deleterious effect on the environment via direct (i.e., trapping longwave radiation) and indirect (altered plant physiology) pathways.[2] Besides, increasing level of CO_2 has also been linked with acidification of sea, and desertification, etc. [3] To circumvent these challenges, recycling of CO_2 into useful feedstock and chemicals have been suggested as the promising solution. [4] In fact, CO_2 serves as an excellent, cheap and abundant building block for obtaining industrially useful C_1 chemicals such as methanol (CH_3OH), formic acid (HCOOH) etc. [5] Despite this, converting CO_2 to the useful chemical products is a daunting task as it is thermodynamically and kinetically uphill process. [6] Therefore, an external source of energy is often employed to reduce CO_2 and various methods have been suggested developed in this direction. Among them, electrochemical reduction (ECR) of CO_2 emerged as an excellent technique due to its rapid nature, low cost and other features. [7] In the last three decades, ECR using transition metal complexes as electrocatalyst have gained an enormous research interest. [8] In literature, various homo- and heterometallic complexes have been reported with low to high activity. [9] It is to be noted that the nature of the reduced product (selectivity) depends on various factors such as solvent, electrolytes etc. Besides, it has also been demonstrated that the illumination of light drives the ECR of CO_2. Based on this knowledge, several photocatalysts and photoelectrodes have been reported in the past. [10] Among them, use of Group IV materials (such Si) for photoelectrochemical reduction of CO_2 known since the last two decades. [11-13] In 2012, Kubiak and co-workers [14] demonstrated visible light-assisted $CO_2 \rightarrow CO$ and $H_2O \rightarrow H_2$ conversion using a combination of homogeneous Re(I) complex a heterogeneous p-Si in non-aqueous medium. Similarly, it was shown that photoelectrocatalytic conversion of $CO_2 \rightarrow CO$ can also be driven at a B-doped, H terminated, p-type S electrode in the presence of a homogenous metalloporphyrin electrocatalyst.[15] Recently, an immense interest have been garnered in the use of metalloporphyrins for electrochemical reduction of hydrogen and CO_2. For example, electrochemical reduction of CO_2 using manganese(III) tetraphenyl porphyrin (Mn(TPP)Cl) as electrocatalyst has been reported with current efficiency ≈ 50- 55%. Among others, the $CO_2 \rightarrow CO$ conversion was the function of type of proton source, amount of catalyst and others. Intrigued by this, present herein is the photoelectrocatalytic performance of a homogenous Mn(TPP)Cl complex for ECR of CO_2 to carbon monoxide (CO) reduction at boron-doped p-type H-terminated silicon.

2. EXPERIMENTS

2.1. Materials and methods

Unless otherwise stated, all chemicals, solvents, Mn(TPP)Cl, and CF_3CH_2OH were purchased from Aldrich (Germany) and used without further purification. Acetonitrile (CH_3CN) was dried by distillation over calcium hydride. Boron-doped p-type H-terminated silicon semiconducting electrode was obtained from Silicon Materials (Germany) and processed as per literature method. [14] Krüss halogen fibre optic lamp ($90 mWcm^{-2}$, $\lambda_{max} = 650$ nm) was used as the source of polychromatic visible light.

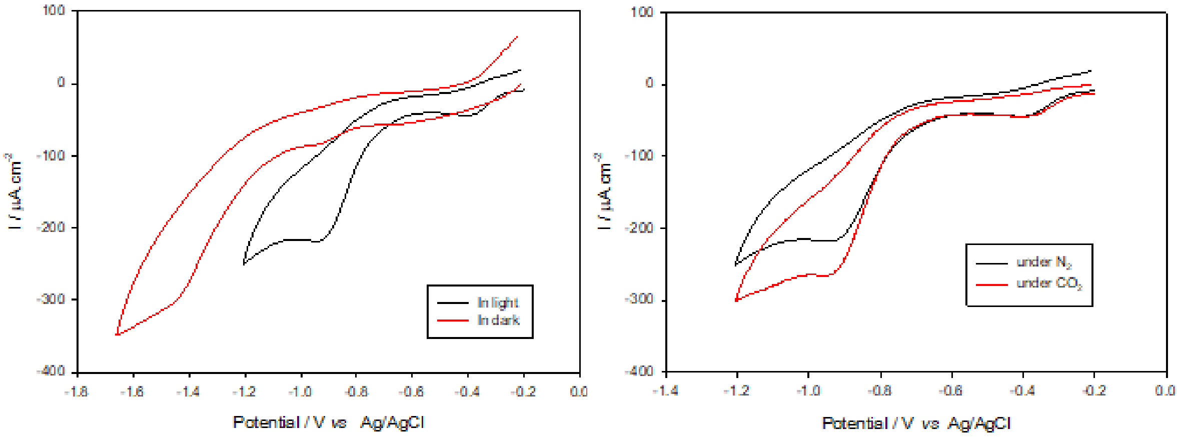
All cyclic voltammetric (CV) experiments were carried out using an Autolab PGSTAT 30 potentiostat equipped with a conventional three-electrode system: a working electrode (vitreous carbon), an auxiliary electrode (platinum wire) and a reference electrode ($Ag^+/AgCl$). To an electrochemical cell containing CH_3CN and electrolyte $[Bu_4N][BF_4]$ (c = 0.1 M, 12 mL) under inert condition, different amount (0.05, 0.5 and 1 mM) of catalyst Mn(TPP)Cl was loaded and stirred to ensure homogenous solution. The CV of Mn(TPP)Cl was collected in the presence and absence of CO_2 in the dark and under the visible light.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry (CV) of Mn(TPP)Cl in dark and under the visible light

The first step was to examine the electrochemical behavior of complex 0.5 mM Mn(TPP)Cl in 0.1 M $[NBu_4][BF_4]$-CH_3CN) under the dark and visible light modes at boron-doped p-type H-terminated silicon. Under the dark condition, two reduction peaks (-1.45 & -1.0 V *vs* Ag/AgCl) observed, which shifted to the positive potentials (-0.90 & -0.50 V *vs* Ag/AgCl) upon irradiation of light, as shown in Fig. 1a. These two reduction waves can be attributed to $Mn^{III} \rightarrow Mn^{II}$ and $Mn^{II} \rightarrow Mn^{I}$ couples, respectively. [15]

Following this, the ECR potential of Mn(TPP)Cl at boron-doped p-type H-terminated silicon electrode under illuminated condition in the absence and presence of CO_2 was also measured (Fig. 1b). The second reduction wave appears to be more than one electron process and the reason could be manifold, i.e. reduction of metal ($Mn^{II} \rightarrow Mn^{I}$), ligand (TPP), or water (solvent) and/catalyst adsorption on the electrode. It was noted that Mn(TPP)Cl, in absence of proton source, interact with the CO_2 near second reduction wave. Possibly in this region, CO_2 reduced to $[MnCO_2]^{3-}$ which subsequently reduced to CO. The catalytic current increase slightly about one and a half time.



(a) **(b)**

Figure 1. CV curves of 0.5 mM Mn(TPP)Cl in $[Bu_4N][BF_4]$-CH_3CN (c = 0.1 M) (a) in dark (red plot) and illuminated (black plot) modes in inert atmosphere, (b) in N_2-(black) and CO_2-saturated (red) electrolyte at boron-doped p-type H-terminated silicon at a scan rate of 100 mV.s^{-1}.

3.2. Effect of Brönsted acid (CF_3CH_2OH) on CV of Mn(TPP)Cl under the visible light

It has been reported that the addition of a Brönsted acid significantly improves the performance (lifetime, efficiency, selectivity) of the catalyst. In this study, we selected trifluoroethanol (CF_3CH_2OH) as the source of proton. Fig. 2a depict the CV curves of 0.5 mM Mn(TPP)Cl in $[Bu_4N][BF_4]$-CH_3CN (c = 0.1 M) in varying amount of Brönsted acid (CF_3CH_2OH) under illuminated condition. It was noted that the presence of CF_3CH_2OH led to a very large catalytic current, supporting the proposition. A catalytic wave near -1.00 V *versus* Ag/AgCl was observed, which was about 2.5 x larger than under CO_2 alone. Upon the addition of > 24 mM of CF_3CH_2OH, the current density reached a saturation and therefore, catalysis become acid independent after this point. Kinetics of photoelectrocatalysis was also investigated. Fig. 2b shows the plot of ratio of peak catalytic current (i_{cat}) to the peak current (i_o) measured for the Mn(II)/Mn(I) reduction step at 100 mVs^{-1} *vs* concentration of CF_3CH_2OH. Analysis of this plot indicate that i_{cat}/i_0 ratio is the function of acid concentration upto 28 mM and then become independent. The rate constant (k_{obs}) at illuminated silicon can be estimated from the i_P / i_P data using the relationship:[17,18]

$$k_{obs} = 0.1992(F\nu/RTn^2)(i_{cat}/i_0)^2 \qquad \text{Eq. 1}$$

where F is Faraday constant, R is gas constant, T is temperature and n is the number of moles of electron.

i_P measured at the potential where the current approaches a plateau at -0.90 V versus Ag/AgCl. The value of k_{obs} is equivalent to the turnover frequency (TOF) of the system and is estimated to be 0.32 x 10^2 s^{-1}, rate constants k_1, was assigned values of 1.28 x10^2 M^{-1} s^{-1}.

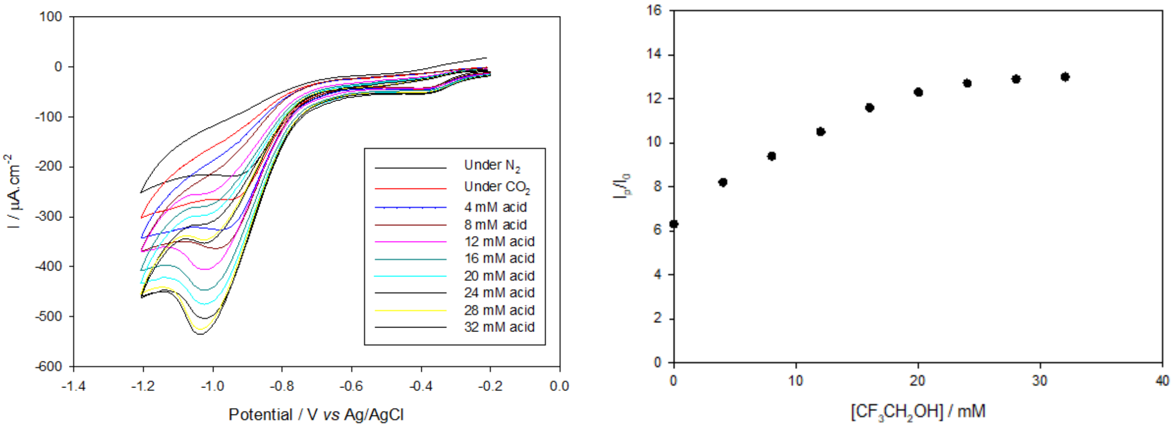


Figure 2. CV of Mn(TPP)Cl (0.5 mM) in MeCN containing 0.1 M $[NBu_4][BF_4]$ at illuminated p-type Si electrode under 1 atm of CO_2 in presence of 4 Mm, 8 Mm, 12 mM,, 12 mM, 16 mM, 20 mM, 24 mM, 28 mM and 32 mM CF_3CH_2OH. Scan rate 100 mVs^{-1}. (b) effect of the CF_3CH_2OH concentration on i_P/i_0 ratio for the Mn(I)/Mn(0) reduction wave at illuminated p-type Si electrode.

3.3. Preparative-Scale Electrolysis at p-type Si electrode

Preparative scale ECR of CO_2 was performed at boron-doped p-type H-terminated silicon and the products were analyzed using GC-MS. Table 1 summaries the results of preparative scale ECR. As it is clear, during 90 mins of photoelectrolysis (0.5 mM catalyst, 32 mM CF_3CH_2OH), the amount of CO produced was 13.2 µmoles (C.E = 48%, -1.00 V *vs* Ag/AgCl, 25 ^{0}C). Besides, H_2 as co-product (C.E. = 42%, 10.4 µmoles) was also observed in somewhat lower quantity. The current vs time shows that the current decrease dramatically after 15 min and the become stable within 36 min , then the current decrease slightly until the current become about 15%. (Fig. 3). It was also noted that the amount of CO and H_2 produced was the function of catalyst loaded. For instance, when the catalyst load was doubled (1.00 mM), the amount of CO increased (C.E. = 53%) while H_2 decreased (C.E. 22 %).

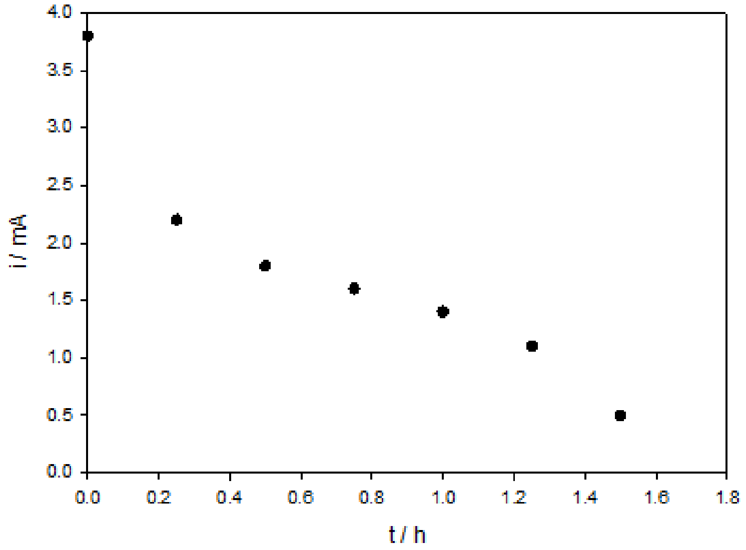


Figure 3. The current versus time: 0.5 mM Mn(TPP)Cl in the presence of CO_2 and 32 mM CF_3CH_2OH in CH_3CN containing 0.1 M $[Bu_4N][BF_4]$ at boron-doped p-type H-terminated silicon.

Table 1. Summary of ECR of CO_2 on preparative scale.

Complex	**Conc /mM**	**charge /C**	**Current efficiency (C.E.) CO %**	**Number of CO /µmol**	**Current efficiency H_2 %**	**Number of H_2 /µmol**
Mn(TPP) Cl	1	6.2	53	17	22	7
	0.5	4.8	48.2	12	42.2	10.5
	0.05	3.6	34.7	6.3	49.3	9.2

Table 2 summarise the result of photoelectrocatalytic experiment performed under similar condition (0.5 mM, 2.5 µ moles of Mn(TPP)Cl and 32 mM CF_3CH_2OH) but for a longer time (100 min). The amount of main and co-products (CO or H_2) generated was measured at regular interval by gas chromatography coupled with mass spectrometer (GC-MS). As is clear from the table, the amount of both the main and co-products (CO or H_2) were the function of electrolysis time. For example, after 20, 40, 60, 80 and 100 mins of electrolysis time, the amount of CO produced was 2.8, 5.7, 7.9, 9.6 and 10.6 µmole, respectively (Fig. 4a). Similar trend was noted for H_2. It is worth mentioning here that the current efficiency (CE) increased during 20 to 80 mins interval and then become stable (for CO) dipped slightly (for H_2) afterwards (Fig. 4b). Control experiment was run at the same condition as above experiment, but in absence of the catalyst and there was no CO detected.

Table 2. The effect of time on ECR of CO_2 on preparative scale.

Time / min		20	40	60	80	100
Number of moles/µmole	CO	2.8	5.7	7.9	9.6	10.6
	H_2	1.8	3.3	5.1	7.2	7.8
Current efficiency (%)	CO	29	38	42.3	45	44.5
	H_2	18	23	27.3	34	32.7
T..N	CO	1.1	2.3	3.2	3.8	4.3
	H_2	1.2	1.6	2.1	2.5	3.1
Charge passed, c		1.9	2.8	3.6	4.1	4.6

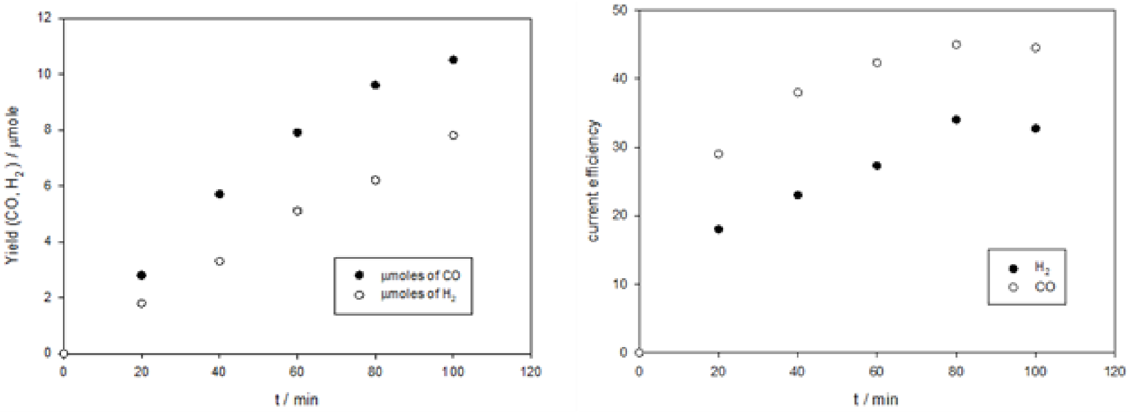


Figure 4. Electrolysis of CO_2 (1 atm) in the presence of Mn(TPP)Cl at boron-doped p-type H-terminated silicon in 0.1M $[Bu_4N][BF_4]$- CH_3CN in the presence of 32 mM CF_3CH_2OH (electrode potential -1 V vs Ag/AgCl at room temperature).

In Table 3, we compare the performance of different metal complexes for ECR of CO_2 reduction at p-type Si electrode. It is clear from the table that the ECR ability of the complex, among others, is the function of both the metal centre and coordinating ligands. In case of Fe, Co, Re and Ni-based complexes, C.E. 22-95% has been reported [15, 19-22]. Not surprising, Re(I) complexes have been reported with very high efficiency [21]. The performance of porphyrin complexes can also be modulated by the coordinating ligand. For instance, fluorinated porphyrins exhibit low C.E. (in case of Fe) while high C.E. in case of Co. In this work, it was noted that non-functionalized TPP-based Mn complex exhibit intermediate performance [23]. In a previous study, it was found that the same complex catalyse the reduction of CO_2 with a slight higher efficiency (~ 50- 55%) on carbon electrode. Similar to this study, nature and amount of the product were found to dependent on the type of acid use. However, in this study, we found a better turn over number.

Table 3. Comparison of the effect of various complexes on CO_2 reduction at p-type Si electrode.

Complex	**Conc. (mM)**	**Potential (V)**	**Reference electrode**	**Current efficiency (CO %)**	**Ref.**
Mn(TPP)Cl	0.5	-1.00	Ag/AgCl	48.2	*This work*
Fe(PFTPP)Cl	0.55	-0.90	Ag/AgCl	22	17
Co(TFPP)	0.35	−1.55	Ag/AgCl	65	18
Fe(TPP)Cl	0.5	-1.2	SCE	90	13
Re(bipy-Bu*t*)(CO)3Cl	0.8	-1.44	Ag/AgCl	97	19
$[(Me6[14]aneN4)NiII]^{2+}$	18	-1.3	SCE	95	20

4. CONCLUSION

In conclusion, the photoelectrochemical CO_2 reduction ability of a homogenous Mn(TPP)Cl complex at p-type silicon semiconducting electrode has been studied. Irradiation of the electrode with polychromatic light shifted to the reduction potentials of Mn(TPP)Cl in DMF containing 0.1M $[NBu_4][BF_4]$ towards the positive potentials. At p-type Si electrode and under illuminated conditions, conversion of CO_2 to CO takes place at a potential *ca* 500 mV positive to that of an inert vitreous carbon electrode with CE of 48.2%. The addition of a weak acid (CF_3CH_2OH) improved the CO_2 reduction process via stabilizing the catalytically active intermediate complex. Besides, hydrogen was also detected as the second major product (CE = 42 %). More H_2 production detected at a lower concentration of catalyst, while the increasing of catalyst concentration let to decrease of production of hydrogen.

References

1. D.S. Reay and J. Grace. Carbon dioxide: Importance, sources and sinks. p. 1-10. In D. Reay (ed.) Greenhouse gas sinks. CAB International, Wallingford, UK (2007).
2. L. Cao, G. Bala, K. Caldeira, R. Nemani and G. Ban-Weiss. *Proc. Nat. Acad. Sci.*, 107 (2010) 9513.
3. G. M. Hallegraeff, *J. Phyco.*, 46 (2010) 220.
4. F. A. Rahman, M. M. A. Aziz, R. Saidur, W. A. W. A. Bakar, M.R. Hainin, R. Putrajaya and N.A. Hassan, *Renew. Sust. Ener. Rev.*, 71 (2010) 112.
5. Y.N. Li, H.R. Li, L.N. He, CO_2 fixation into organic molecules via carbon–heteroatom bond formation. P. 155-198. In S. Das (ed.) CO_2 as a Building Block in Organic Synthesis (2020).
6. X. Zhu, Q. Imtiaz, F. Donat, C.R. Müller and F. Li, *Ener. Env. Sci.*, 13 (2020) 772.
7. F. Zhang, H. Zhang and Z Liu, *Curr. Opin. Green Sustain. Chem.,* 16 (2019) 77.
8. D.M. Feng, Y.P. Zhu, P. Chen and T.Y. Ma, *Catalysts*, 7 (2017) 373.
9. N.W. Kinzel, C. Werlé and W. Leitner, *Angew. Chem. Int. Ed.*, 60 (202) 11628.
10. J.L. White, M.F. Baruch, J.E. Pander, Y. Hu, I.C. Fortmeyer, J.E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T.W. Shaw, E. Abelev and A.B. Bocarsly, *Chem. Rev.,* 23 (2015) 12888.
11. I. Taniguchi, B. Aurian-Blajeni, and B. Jo'm, *Electrochimica acta*, 29 (1984) 923
12. B. Aurian-Blajeni, I. Taniguchi, and B. Jo'm, *J. Electroanal. Chem. Interfac. Electrochem.*, 149(1983) 291;
13. V. Guruswamy, and J. Bockris, J., *Int. J. Ener. Res.*, *3* (1979) 397.
14. B. Kumar, J. M.Smieja, A.F. Sasayama and C.P. Kubiak, *Chem. Comm.*, 48 (2012), 272.

15. K. Alenezi, S. K. Ibrahim, P. Li and C.J. Pickett, *Chem. Euro. J.*, 40 *(*2013) 13522.
16. R. N. Dominey, N. S. Lewis, J. A. Bruce, D. C. Bookbinder and M.S. Wrighton. *J. Am. Chem. Soc*. 104 (1982) 467.
17. D. L. DuBois, *Inorg. Chem.,* 53 (2014), 3935.
18. M. Rakowski Dubois and D. L. Dubois, *Acc. Chem. Res.* 42 *(*2009), 1974.
19. K. Alenezi, *Int. J. Electro. Sci*. 10 (2015), 4279.
20. K. Alenezi, *J. Chem*., (2016), 1501728.
21. B. Kumar, J. M.Smieja and C.P. Kubiak, *J. Phys. Chem. C*, 114 (2010), 14220.
22. M.G. Bradley, T. Tysak, D. J. Graves and N.A. Viachiopoulos, *J. Chem. Soc. Chem. Comm*., 7 (1983), 349.
23. K. M. Alenezi, *Croatica Chemica Acta*, 93 (2020) 41.