

# NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

## Recent Advances on Catalytic CO<sub>2</sub> Reduction by Organometal Complexes Anchored on Modified Electrodes

Cunfa Sun,<sup>a</sup> Roberto Gobetto<sup>a\*</sup> and Carlo Nervi<sup>a\*</sup>

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Critical overview of the very recent literature on heterogeneous electrochemical catalysis of CO<sub>2</sub> reduction with organic metal modified electrodes is summarized. Five methods for electrode functionalization are discussed and compared in terms of efficiency and selectivity: adsorption, by using membranes, adopting an “hybrid” covalent organic framework approach, performing electropolymerization directly on the electrode surface, and exploiting the formation of strong covalent chemical bonds between the surface and the desired catalyst.

### Introduction

The catalytic conversion of the extremely stable CO<sub>2</sub> molecule to usable fuels or chemical products is a critical goal that would positively impact the global environment and hopefully helping in overcoming some of the problems of energy crisis.<sup>1-6</sup> Valuable products, such as carbon monoxide, formic acid and high-molecular-weight polymers, obtained from the electrochemical conversion of CO<sub>2</sub>, have been indicated as chemicals that can store intermittent energy sources, thus balancing power supply and energy demand and environmental concerns of greenhouse gas emissions. A possible approach to reduce the large overpotentials required for this multi-electron process is the use of organometal molecular compounds, able to catalyze CO<sub>2</sub> reduction through proton-assisted processes.<sup>4, 7</sup> Most electrocatalytic studies in this field focus primarily on the catalyst/substrate interaction in homogeneous solution. Relatively few works were focused on the heterogeneous electrochemical catalysis despite the large number of potential advantages such as easier recovery of products and catalyst, small amounts of catalyst necessary for efficient electrolysis, deactivation pathways often hindered or suppressed and elimination of solubility problems. Furthermore, in heterogeneous system the electron transfer will be more efficient to the attached or bonded catalyst compared with that in solution, lowering the limitation of the electron transfer in the catalytic cycle. Transition metal complexes immobilized on electrode surfaces can represent promising catalysts to be utilized on a large-scale process for CO<sub>2</sub> reduction, particularly if non-precious metals like cobalt, iron, nickel, copper, and zinc are involved. Although the interest in this area began several decades ago, it has drawn substantial attention only in the recent years, due to the development of photoelectrochemical (PEC)

cells dedicated to CO<sub>2</sub> reduction, currently one of the most popular topic.<sup>6</sup> PEC cell design is a complex matter and involves simultaneous managing of a multitude of processes related to solar excitation, charge separation, electrical conduction, molecular transport, catalytic chemistry, and reaction product recovery. Progress in this field have been made, especially for H<sub>2</sub>O reduction,<sup>8,9</sup> but PECs for CO<sub>2</sub> reduction are still in their infancy. An interesting review on modified electrodes by anchoring transition metal complexes as catalyst for CO<sub>2</sub> reduction has been published some years ago by Vos and coworkers.<sup>10</sup> Nevertheless the field is so rapidly growing both in interest and importance that a critical overview of the recent results is desirable. In this focus we present a brief overview of the most important recent results of such modified electrodes as electrocatalysts for CO<sub>2</sub> reduction by different methods of anchoring transition metal complexes on the electrodes.

### Electrode functionalization by adsorption

Among the different techniques for immobilizing the catalysts onto the electrode surface, chemisorption certainly represents one of the most convenient method.<sup>11-13</sup> Catalyst molecules bearing special moieties such as aromatic group or double bonds, etc. show chemical affinity to form spontaneously non covalent modification of electrode surfaces enough stable for long periods in solvents where they are insoluble. Meshitsuka and coworkers<sup>14</sup> in 1974 published the first attempt to perform heterogeneous CO<sub>2</sub> electrocatalysis by phthalocyanine (Pc) metal (Mn, Pd, Cu, Fe, Co, Ni) complexes (MPC) adsorbed on graphite electrode surface; Co(Pc) proved to be one of the most reactive catalysts for CO<sub>2</sub> electroreduction. After the seminal work of Lehn and coworkers<sup>15</sup> that introduced bipyridyl Re complex into CO<sub>2</sub> electrocatalysis, many efforts have been performed with these complexes due to their higher selectivity compared with other catalysts. However the first paper of non-covalent surface attachment of a bipyridyl Re mo-

<sup>a</sup> Department of Chemistry, NIS and CIRCC (Bari) University of Torino via P. Giuria 7, 10125 Torino, Italy.

lecular complex for catalytic CO<sub>2</sub> reduction appeared only in 2013.<sup>16</sup> A graphite electrode was modified with a Re complex containing pyrene groups that sticks on the graphite electrode through a π-π stacking interaction. At a rather negative applied potential, -1.67 V vs NHE (Normal Hydrogen Electrode), in acetonitrile, the modified electrode shows CO faradaic efficiency ( $\eta_{CO}$ , defined as the moles of electrons consumed to get the desired reaction product divided by the total moles of electrons transferred from anode to cathode<sup>6</sup>) = 70% and TON<sub>CO</sub> = 58 with no H<sub>2</sub> formation (TON = Turn Over Number, defined as the moles of intended reaction product formed divided by the moles of catalytic sites). Functionalized surface lost its activity after 1 h due to the reduction of the pyrenyl moieties at the very negative potentials, probably due to electrostatic repulsion with the surface and consequent loss of planarity and surface binding.

Compared to CO<sub>2</sub> reduction by one-electron process, proton coupled multi-electron reduction requires less overpotential.<sup>10, 17</sup> An ITO/multilayer electrode<sup>18</sup> was modified by the Layer-by-Layer method (LBL) with corresponding multimetallic complex, Mn(III)/Ni(II)/Zn(II) μ-(meso-5,10,15,20-tetra(pirydil)porphyrin) tetrakis [bis (bipyridine) chloride ruthenium(II)] ([MTRP]<sup>n+</sup> (Fig. 1; M = Mn(III), Ni(II) and Zn(II), n = 5, 4, 4 respectively)), and polyoxotungstate ([SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup>). By performing electrolysis at -0.8 V vs. Ag/AgCl for 6 h in aqueous solution, CO was the only product on [ZnTRP]<sup>n+</sup>/[SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> multilayer electrode with TON<sub>CO</sub> = 3850, while the analogues [NiTRP]<sup>4+</sup>/[SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> and [MnTRP]<sup>5+</sup>/[SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> produced methanol (TON<sub>MeOH</sub> = 1.76 × 10<sup>5</sup>) and formic acid (TON<sub>HCOOH</sub> = 1.06 × 10<sup>6</sup>), respectively. It is worth noting in the energy transfer of the TRP that extra irradiation altered the catalysis pathway and lowered the potential, enhancing the catalytic efficiency. At -0.6 V vs. Ag/AgCl under irradiation, [MnTRP]<sup>5+</sup>/[SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> produced formaldehyde only with TON<sub>HCHO</sub> = 1.8 × 10<sup>5</sup>.

With the help of polyethyleneimine and high surface area multi-walled carbon nanotubes (MWCNT), Zhao and coworkers<sup>19</sup> were able to produce cobalt tetra-amino-phthalocyanine (CoTAPc) modified electrodes with multilayers by using LBL self-assembly technique. The new electrodes significantly decreased the overpotential of the CO<sub>2</sub> reduction, and the cathode successfully reduced CO<sub>2</sub> to formic acid. MWCNT/CoTAPc modified electrode produced twice number of moles of formic acid than the electrode without MWCNT. Later, they reported a glassy carbon (GC) or carbon felt electrode functionalized with MWCNT/FeTAPc, showing catalysis at less negative potential and higher reaction rate than the electrode with only MWCNT or FeTAPc.<sup>20</sup>

### Electrode functionalization by membrane

Polymeric matrices which could confine the catalyst in a membrane attached onto the electrode surface provides another convenient way for electrode modification. The electrochemical reaction takes place in the membrane-electrode-catalyst layers and requires high proton and electron conductivity, and effective access of reactants to the catalyst. Preliminary inves-

tigation in this field have been reported by Yoshida and coworkers<sup>21</sup> that studied the catalytic activity towards CO<sub>2</sub> reduction in aqueous solution of [Co(tpy)<sub>2</sub>]<sup>2+</sup> (tpy = 2,2':6',2''-terpyridine) on Nafion coated

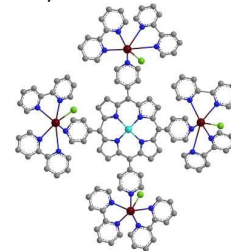


Figure 1. Structural representation of [MTRP]<sup>n+</sup> (M = Mn(III), Ni(II) and Zn(II), n = 5, 4, 4 respectively)<sup>18</sup>.

carbon electrodes. Re(bpy)(CO)<sub>3</sub>Br and Re(tpy)(CO)<sub>3</sub>Br (bpy = 2,2'-bipyridine, tpy = 2,2':6',2''-terpyridine) coated on Nafion membranes in aqueous solution showed higher selectivity,<sup>22</sup> but strongly dependent on the applied potentials. In particular Re(tpy)(CO)<sub>3</sub>Br complex produces mainly formic acid and requires larger overpotential than the bpy analogous.

As a substitute of Re, bipyridyl Mn complexes shows excellent selectivity in CO<sub>2</sub> with<sup>23</sup> and without<sup>24</sup> added Brønsted acid. In 2014 Cowan's group<sup>25</sup> embedded [Mn(bpy)(CO)<sub>3</sub>Br] in a Nafion membrane as an active heterogeneous electrocatalyst for CO<sub>2</sub> reduction in neutral aqueous electrolyte at less negative potential compared with the homogeneous solution. Although the number of active catalytic molecules were rather limited in the membrane, TON reached 471 (~36 fold higher than the homogeneous counterpart<sup>23</sup>),  $\eta_{CO}$  = 51% and  $\eta_{H_2}$  = 24% after 4 hours at -1.5 V vs. Ag/AgCl. The [Mn(bpy)(CO)<sub>3</sub>Br]/MWCNT/Nafion electrode leads to a 10 fold current enhancement, but with lower TON value (101) and lower selectivity ( $\eta_{CO}$  = 22%,  $\eta_{H_2}$  = 47%). Very recently, they immobilized [Mn(bpy(<sup>t</sup>Bu)<sub>2</sub>)(CO)<sub>3</sub>Br]<sup>26</sup> (bpy(<sup>t</sup>Bu)<sub>2</sub> = 4,4'-di-tert-butyl-2,2'-bipyridine) on GC by Nafion/MWCNT. This film improved the selectivity towards CO<sub>2</sub> at -1.4 V vs. SCE ( $\eta_{CO}$  = 44%,  $\eta_{H_2}$  = 46%), exceeding that of the previously reported [Mn(bpy)(CO)<sub>3</sub>Br]/MWCNT/Nafion electrode. The catalysts obtained by replacing bpy with 4,4'-dicarboxylic acid bpy or with 4,4'-diol bpy were found to be active towards CO<sub>2</sub> in acetonitrile solutions, but not in Nafion membranes. Aoi and coworkers<sup>27</sup> studied the CO<sub>2</sub> reduction with a GC electrode modified by a CoCl<sub>2</sub> complex, Co<sup>II</sup>(Ch), adsorbed on MWCNT confined in Nafion (Fig. 2). At -1.1 V vs. NHE in aqueous solution in pH 4.6 buffer, the system yielded CO and H<sub>2</sub> as major products with TON = 1100 (with a Turn Over Frequency, TOF, defined as TON divided by the reaction time, equal to 140 h<sup>-1</sup>)  $\eta_{CO}$  = 89%,  $\eta_{H_2}$  = 11%.

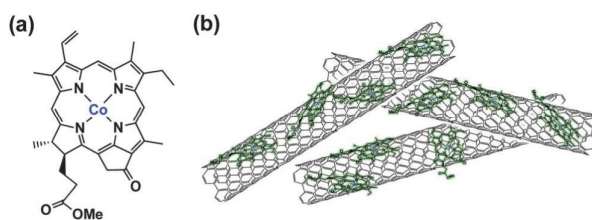


Figure 2. (a) Structure of  $\text{Co}^{\text{II}}(\text{Ch})$  and (b) schematic image of  $\text{Co}^{\text{II}}(\text{Ch})$  on MWCNTs<sup>27</sup>.

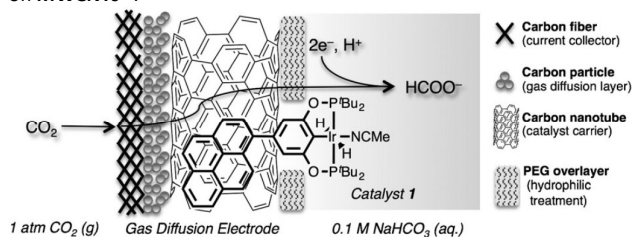


Figure 3. Carbon nanotube-coated gas diffusion electrode, with Ir pin-core dihydride catalyst bounded on the surface for electrochemical reduction of  $\text{CO}_2$  to formate<sup>28</sup>.

Gas diffusion electrode (GDE) promotes catalytic  $\text{CO}_2$  reduction in solution at gas-liquid interface.<sup>29</sup> Meyer's group<sup>28</sup> reported GDE/MWCNT/Ir/PEG system (Ir = iridium catalyst, see Fig. 3, PEG = polyethylene glycol) for  $\text{CO}_2$  reduction, where the catalyst was non-covalently adsorbed on the MWCNT, and covered by PEG on the top of the surface. Also, the GC and the fluorine-doped tin oxide (FTO) electrodes were investigated for comparison. The GDE system showed a little better TON than others, while the GC system exhibited  $\eta_{\text{HCOO}^-} = 93\%$ ,  $\text{TON} = 5300$  in 2 h at  $-1.4$  V vs. NHE in aqueous solution with  $\eta_{\text{H}_2} = 7\%$ , and  $\text{TON} = 203000$  in 8 h, which is about four orders of magnitude higher than homogeneous solution<sup>30</sup>. By using a membrane, anchoring the catalyst becomes easier, and the catalysis can be directly tested. Singh and coworkers<sup>31</sup> tested the  $\text{CO}_2$  reduction catalytic activity of Ni and Cu salen ligand complexes directly applied with Nafion coated on GDE. These salen ligand complexes showed long stability and produced more quantity of hydrocarbons and CO at a 10-25% less overpotential than their respective metals, with total  $\eta$  of 74% for Ni complex and 25% for Cu complex at  $-1.5$  V and  $-1.8$  V vs. Ag/AgCl, respectively. The catalyst (N,N-Bis(salicylidene)-ethylenediamine-Co) was dispersed in carbon black,<sup>32</sup> and the mixture was covered with Nafion over GDE. The electrode with 60wt% exhibited the best activity for  $\text{CO}_2$  reduction in aqueous solution, due to the right balance of porosity and conductivity of the carbon black mixture.

### Electrode modification by covalent organic frameworks (COF)

Without the membrane support, catalyst can also be physically compacted on the rough electrode surface. Very recently Yaghi and coworkers<sup>33, 34</sup> reported cobalt porphyrin catalysts on COFs, bridged by organic struts via functional groups. The microcrystalline COF formed automatically on alumina coated fluorine-doped tin oxide (FTO)<sup>34</sup> or the powders were directly deposited on porous conductive carbon fabric for aqueous electrochemical reduction of  $\text{CO}_2$ . The catalysts exhibited high  $\eta_{\text{CO}}$  and  $\text{TON}_{\text{CO}}$ , and long stabilities. The microcrystalline COF deposited on carbon fabric<sup>33</sup> showed larger porous, more dispersed Co centers and higher TON, but lower selectivity and lower  $\eta_{\text{CO}}$ , and it suffered low active sites' ratio (4% of the total catalyst on the surface) caused by aggregation. Even though,

they are among the most active catalysts (Fig. 4) with  $\text{TON}_{\text{CO}} \approx 48000$  per active site in 24 h with  $\eta_{\text{CO}} = 83\%$  and  $\eta_{\text{H}_2} = 24\%$ .

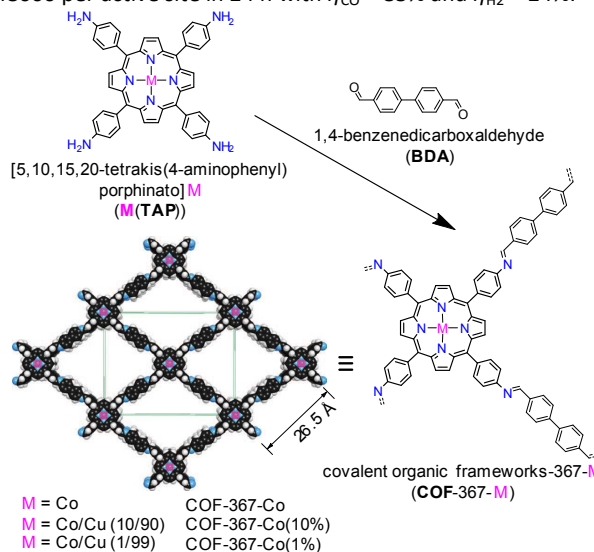


Figure 4. Design and synthesis of metalloporphyrin-derived 2D covalent organic frameworks<sup>33</sup>.

### Electrode functionalization by electropolymerization

If the catalyst bears a suitable group able to polymerize, the electrode surface can be easily modified by electropolymerization.<sup>35, 36</sup> Portenkirchner and coworkers<sup>37, 38</sup> electropolymerized a 5,5'-bisphenylethynyl bipyridyl Re complex on the electrode surface, as a potential catalyst for  $\text{CO}_2$  reduction. However, the homogeneous and the heterogeneous catalyst showed in  $\text{CH}_3\text{CN}$  solutions relative low  $\eta_{\text{CO}}$  for  $\text{CO}_2$  reduction, 45% and 33% respectively. We very recently exploited the electropolymerization properties of Re(bpy) complexes containing the thiophene moiety, that have the advantage to produce an electron-conducting film, with interesting results.<sup>39</sup>

The electrocatalytic reduction of  $\text{CO}_2$  on a ITO electrode covered with cobalt 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (Co-TAPP) polymer in 1-butyl-3-methylimidazolium tetrafluoroborate,  $\text{BMImBF}_4$ ) as a novel reaction media,<sup>40</sup> occurred at a particularly positive potential,  $-0.8$  V vs. Ag/AgCl, which means a significant energy gain in the electrochemical fixation of  $\text{CO}_2$ . Only CO was detected by gas chromatography, with  $\eta_{\text{CO}} = 64.9\%$  and  $\text{TON} = 69$  for 4 h. Later, Zn(II) and Fe(III) were used as catalysts with the same procedure,<sup>41</sup> but while the electropolymerized Fe porphyrin was active toward  $\text{CO}_2$  reduction, the corresponding Zn derivative was poorly active.

### Electrode functionalization by chemical bonds

Formation of covalent chemical bonds between the catalyst and the surface impart particular stability to the modified electrodes. Cobalt porphyrin complexes bearing peripheral acetylene groups was covalently linked to the boron-doped p-type



conductive crystalline diamond electrode surface decorated with alkyl azides.<sup>42</sup> The modified diamond surface was used as “smart” electrode, exhibiting good stability and electrocatalytic activity for CO<sub>2</sub> reduction to CO in acetonitrile solution.

Very recently, the electrochemical behavior of a GC prepared by simple and direct functionalization of terpyridine containing diazonium salts was explored.<sup>43</sup> This versatile strategy allows to extend the use of such modified electrodes through the reversible coordination of a variety of metal ions; for example cobalt center have been tested for the CO<sub>2</sub> reduction, with TON<sub>co</sub> = 70 for 30 min.<sup>43</sup>

Please Insert Table 1 (that contains Ref. <sup>44</sup>) around here

## Conclusions

Table 1 summarizes the properties of the electrodes herein considered. Often organic metal complexes anchored on modified electrodes exhibit better Turn Over Number, faradic efficiencies, stability, and/or less negative overpotentials compared with the corresponding complexes in homogeneous solution, highlighting the beneficial effect of the immobilization. Physical attachment of catalysts on the surface by Nafion, polymer membrane or nanoparticles etc., would have the drawback of lower number of active sites on the surface (because part of the catalyst embedded in the solid structure may be hidden to the reaction), while monolayer of covalently chemically bonded species or adsorbed polymer, produced also by electropolymerization, have less total amount, but potentially better electron conduction properties. Although no general rule can be suggested at this stage of the research, the best solution appears to adopt electrodes with the largest surface area, in order to maximize the amount of active catalyst in contact with the reactive interface. Hence, the new electrode modification methods by novel hybrid electrode material via covalent organic framework approach seems quite promising. The challenge is to provide an adequate transport of materials (to and from the catalytic center) and electrons (via a conductive material) to the active surface.

The recent works suggested that dispersed catalyst could exhibit much better activity than the concentrated ones, such as the complexes with pores or localized in the porous matrix. That may arise from the more free catalytic environment around the catalyst center, or because reaction products may interfere with the catalytic cycle. The Gas Diffusion Electrode approach that adopt the conductive black carbon is also appealing, due to the gaseous nature of CO<sub>2</sub> that would allow the direct reaction without the need to use an organic solvent for CO<sub>2</sub> solutions. Thus the Covalent Organic Framework and Gas Diffusion Electrode approaches are actually the most efficient ones in term of TON, selectivity, and durability, and appear to be suitable to be embedded in a Photo Electrochemical Cell for CO<sub>2</sub> reduction.

From this point of view the research field appears to be promising and mostly unexplored, when compared to the homogeneous counterpart. The use of intact transition metal com-

plexes anchored to conducting surface appear to be one of the main research fields that would allow a competitive development of Photo Electrochemical solar cell for selective CO<sub>2</sub> conversion, allowing the molecular design of the catalysts. Investigation of proton assisted multi-electron reduction in different solvents, may significantly alter the selectivity, and it seems to be the preferred pathway to follow, due to benefits in decreasing the reduction overpotentials and increasing selectivity.

Although, a lot of efforts have been done in the heterogeneous CO<sub>2</sub> reduction, the elucidation of the mechanism is still obscure compared with the homogeneous, and the catalytic pathways seldom discussed, even there's some works that mention the use of Infrared<sup>45</sup> or Electrochemical Impedance Spectroscopy<sup>40</sup>. The knowledge of the mechanism will certainly help the design of more efficient catalysts and systems. So there are a plenty of research opportunities ranging from molecular or solid state calculations, in *in-situ* spectroscopic techniques, and especially electrochemical techniques that allow to study the chemical reaction at the interfaces.

## Notes and references

1. E. E. Benson, C. P. Kubiak, A. J. Sathrum and J. M. Smieja, *Chem. Soc. Rev.*, 2009, **38**, 89-99.
2. W. Wang, S. Wang, X. Ma and J. Gong, *Chem. Soc. Rev.*, 2011, **40**, 3703-3727.
3. A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer and G. L. Waldrop, *Chem. Rev.*, 2013, **113**, 6621-6658.
4. C. Costentin, M. Robert and J.-M. Saveant, *Chem. Soc. Rev.*, 2013, **42**, 2423-2436.
5. J. Qiao, Y. Liu, F. Hong and J. Zhang, *Chem. Soc. Rev.*, 2014, **43**, 631-675.
6. J. Ronge, T. Bosserez, D. Martel, C. Nervi, L. Boarino, F. Taulelle, G. Decher, S. Bordiga and J. A. Martens, *Chem. Soc. Rev.*, 2014, **43**, 7963-7981.
7. J.-M. Saveant, *Chem. Rev.*, 2008, **108**, 2348-2378.
8. M. G. Mali, H. Yoon, B. N. Joshi, H. Park, S. S. Al-Deyab, D. C. Lim, S. Ahn, C. Nervi and S. S. Yoon, *ACS Appl. Mater. Interfaces*, 2015, **7**, 21619-21625.
9. M. T. Mayer, Y. J. Lin, G. B. Yuan and D. W. Wang, *Acc. Chem. Res.*, 2013, **46**, 1558-1566.
10. J. L. Inglis, B. J. MacLean, M. T. Pryce and J. G. Vos, *Coord. Chem. Rev.*, 2012, **256**, 2571-2600.
11. R. W. Murray, *Acc. Chem. Res.*, 1980, **13**, 135-141.
12. R. W. Murray, A. G. Ewing and R. A. Durst, *Anal. Chem.*, 1987, **59**, 379a-390a.
13. A. J. Bard, *J. Chem. Educ.*, 1983, **60**, 302-304.
14. S. Meshitsuka, M. Ichikawa and K. Tamaru, *J. Chem. Soc., Chem. Commun.*, 1974, 158-159.
15. J. Hawecker, J. M. Lehn and R. Ziessel, *J. Chem. Soc., Chem. Commun.*, 1984, 328-330.
16. J. D. Blakemore, A. Gupta, J. J. Warren, B. S. Brunshwig and H. B. Gray, *J. Am. Chem. Soc.*, 2013, **135**, 18288-18291.
17. H. Takeda and O. Ishitani, *Coord. Chem. Rev.*, 2010, **254**, 346-354.

18. M. Garcia, M. Jesus Aguirre, G. Canzi, C. P. Kubiak, M. Ohlbaum and M. Isaacs, *Electrochim. Acta*, 2014, **115**, 146-154.
19. H. Z. Zhao, Y. Zhang, B. Zhao, Y. Chang and Z. Li, *Environ. Sci. Technol.*, 2012, **46**, 5198-5204.
20. H. Z. Zhao, Y.-Y. Chang and C. Liu, *J. Solid State Electrochem.*, 2013, **17**, 1657-1664.
21. T. Yoshida, T. Iida, T. Shirasagi, R. J. Lin and M. Kaneko, *J. Electroanal. Chem.*, 1993, **344**, 355-362.
22. T. Yoshida, K. Tsutsumida, S. Teratani, K. Yasufuku and M. Kaneko, *J. Chem. Soc., Chem. Commun.*, 1993, 631-633.
23. M. Bourrez, F. Molton, S. Chardon-Noblat and A. Deronzier, *Angew. Chem. Int. Ed.*, 2011, **50**, 9903-9906.
24. F. Franco, C. Cometto, F. Ferrero Vallana, F. Sordello, E. Priola, C. Minerio, C. Nervi and R. Gobetto, *Chem. Commun.*, 2014, **50**, 14670-14673.
25. J. J. Walsh, G. Neri, C. L. Smith and A. J. Cowan, *Chem. Commun.*, 2014, **50**, 12698-12701.
26. J. J. Walsh, C. L. Smith, G. Neri, G. F. Whitehead, C. M. Robertson and A. J. Cowan, *Faraday Discuss.*, 2015, DOI: 10.1039/c5fd00071h.
27. S. Aoi, K. Mase, K. Ohkubo and S. Fukuzumi, *Chem. Commun.*, 2015, **51**, 10226-10228.
28. P. Kang, S. Zhang, T. J. Meyer and M. Brookhart, *Angew. Chem. Int. Ed.*, 2014, **53**, 8709-8713.
29. R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K.-i. Kimijima and N. Iwashita, *Chem. Rev.*, 2007, **107**, 3904-3951.
30. P. Kang, C. Cheng, Z. Chen, C. K. Schauer, T. J. Meyer and M. Brookhart, *J. Am. Chem. Soc.*, 2012, **134**, 5500-5503.
31. S. Singh, B. Phukan, C. Mukherjee and A. Verma, *Rsc Advances*, 2015, **5**, 3581-3589.
32. Y. Fu, Y. Liu, Y. Li, J. Li, J. Qiao and J. Zhang, *J. Solid State Electrochem.*, 2015, **19**, 3355-3363.
33. S. Lin, C. S. Diercks, Y.-B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi and C. J. Chang, *Science*, 2015, **349**, 1208-1213.
34. N. Kornienko, Y. Zhao, C. S. Kley, C. Zhu, D. Kim, S. Lin, C. J. Chang, O. M. Yaghi and P. Yang, *J. Am. Chem. Soc.*, 2015, **137**, 14129-14135.
35. T. R. Otoole, L. D. Margerum, T. D. Westmoreland, W. J. Vining, R. W. Murray and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1985, 1416-1417.
36. A. R. Guadalupe, D. A. Usifer, K. T. Potts, H. C. Hurrell, A. E. Mogstad and H. D. Abruna, *J. Am. Chem. Soc.*, 1988, **110**, 3462-3466.
37. E. Portenkirchner, K. Oppelt, C. Ulbricht, D. A. M. Egbe, H. Neugebauer, G. Knoer and N. S. Sariciftci, *J. Organomet. Chem.*, 2012, **716**, 19-25.
38. E. Portenkirchner, J. Gasiorowski, K. Oppelt, S. Schlager, C. Schwarzinger, H. Neugebauer, G. Knoer and N. S. Sariciftci, *ChemCatChem*, 2013, **5**, 1790-1796.
39. C. Sun, S. Prosperini, P. Quagliotto, G. Viscardi, S. S. Yoon, R. Gobetto and C. Nervi, *Dalton Trans.*, 2016, DOI: 10.1039/C5DT04491J.
40. D. Quezada, J. Honores, M. Garcia, F. Armijo and M. Isaacs, *New J. Chem.*, 2014, **38**, 3606-3612.
41. D. Quezada, J. Honores, M. Jesus Aguirre and M. Isaacs, *J. Coord. Chem.*, 2014, **67**, 4090-4100.
42. S. A. Yao, R. E. Ruther, L. Zhang, R. A. Franking, R. J. Hamers and J. F. Berry, *J. Am. Chem. Soc.*, 2012, **134**, 15632-15635.
43. N. Elgrishi, S. Griveau, M. B. Chambers, F. Bedioui and M. Fontecave, *Chem. Commun.*, 2015, **51**, 2995-2998.
44. V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, 2000, **298**, 97-102.
45. P. Christensen, A. Hamnett, A. V. G. Muir, J. A. Timney and S. Higgins, *J. Chem. Soc. Faraday Trans.*, 1994, **90**, 459-469.

**Table 1.** Comparison of modified electrode performances for catalytic CO<sub>2</sub> electrochemical reductions in MeCN solutions (0.1 M TBAPF<sub>6</sub>).

Method	Electrode/(catalyst)	E (V)	E (V) <sup>a</sup> vs. NHE	η <sub>CO</sub> (%)	TON <sub>CO</sub>	Time (h)	Solution	Ref
Adsorption	graphitic carbon electrode/([Re(P)-(CO) <sub>3</sub> Cl])	-1.67 vs NHE	-1.67	70	58	1	0.1M TBAPF <sub>6</sub> MeCN	<sup>16</sup>
	ITO/([ZnTRP] <sup>2+</sup> /[SiW <sub>12</sub> O <sub>40</sub> ] <sup>4-</sup> )	-0.8 vs Ag/AgCl	-0.51	---	3850	6	0.1 M NaClO <sub>4</sub>	<sup>18</sup>
	ITO/([NiTRP] <sup>4+</sup> /[SiW <sub>12</sub> O <sub>40</sub> ] <sup>4-</sup> )	-0.8 vs Ag/AgCl	-0.51	---	1.76×10 <sup>5 a</sup>	6	0.1 M NaClO <sub>4</sub>	<sup>18</sup>
	ITO/[MnTRP] <sup>5+</sup> /[SiW <sub>12</sub> O <sub>40</sub> ] <sup>4-</sup> )	-0.8 vs Ag/AgCl	-0.51	---	1.06×10 <sup>6 b</sup>	6	0.1 M NaClO <sub>4</sub>	<sup>18</sup>
	ITO/ ([MnTRP] <sup>5+</sup> /[SiW <sub>12</sub> O <sub>40</sub> ] <sup>4-</sup> ) <sup>c</sup>	-0.65 vs Ag/AgCl	-0.36	---	1.86×10 <sup>5 d</sup>	3	0.1 M NaClO <sub>4</sub>	<sup>18</sup>
Membrane	GCE/([Mn(bpy)(CO) <sub>3</sub> Br])	-1.50 vs Ag/AgCl	-1.21	51 24 <sup>e</sup>	471	4	phosphate buffer pH≈7	<sup>25</sup>
	GCE/([Mn(bpy)(CO) <sub>3</sub> Br]/MWCNT)	-1.50 vs Ag/AgCl	-1.21	22 47 <sup>e</sup>	101	4	phosphate buffer pH≈7	<sup>25</sup>
	GCE/([Mn(bpy <sup>t</sup> Bu) <sub>2</sub> (CO) <sub>3</sub> Br]/MWCNT)	-1.40 vs. SCE	-1.07	44 46 <sup>e</sup>	7.3	4	phosphate buffer pH≈7	<sup>26</sup>
	GCE/([Co <sup>II</sup> (Ch)]/MWCNT)	-1.10 vs. NHE	-1.10	89 11 <sup>e</sup>	1100	8	5 mM NaClO <sub>4</sub> pH=4.6 <sup>f</sup>	<sup>27</sup>
	GDE/ (Ir/MWCNT)	-1.40 vs. NHE	-1.40	93 <sup>g</sup>	5300 <sup>g</sup>	2	0.1m NaHCO <sub>3</sub> , 0.5m LiClO <sub>4</sub> , 1% MeCN v/v	<sup>28</sup>
COF	carbon fabric/(COF-367-Co)	-1.30 vs. Ag/AgCl	-1.01	83 24 <sup>e</sup>	48000	24	0.5 M KHCO <sub>3</sub> pH=7.3	<sup>33</sup>

## ARTICLE

## Journal Name

electropolymerization	FTO/(Al <sub>2</sub> (OH) <sub>2</sub> TCPP-Co) <sup>h</sup>	-1.33 vs. Ag/AgCl	-1.04	76	1400	7	0.5 M KHCO <sub>3</sub>	34
	Pt-plate /([Re(5,5'-bisphenylethynyl-2,2'-bipyridyl)(CO) <sub>3</sub> Cl])	-1.6 vs. NHE	-1.60	33	---	1	0.1M TBAPF <sub>6</sub> MeCN	38
Chemical bond	ITO/(Co-TAPP)	-0.8 vs. Ag/AgCl	-0.51	64.9	69	4	BMI <sub>4</sub> BF <sub>4</sub>	40
	GCE/Co-tpy	-1.50 vs. Ag/AgCl	-1.21	---	70	0.5	0.1 M TBAPF <sub>6</sub> DMF	43

a) TON<sub>MeOH</sub>; b) TON<sub>HCOOH</sub>; c) under irradiation; d) TON<sub>HCOOH</sub>; e) TON<sub>H<sub>2</sub></sub>; f) adjusted by H<sub>2</sub>SO<sub>4</sub> aqueous solution; g) formate; h) TCPP-H<sub>2</sub> = 4,4',4''-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate. i) the redox potentials are reported against NHE for comparison, using the value in Ref.<sup>44</sup>

Critical overview of the very recent literature on heterogeneous electrochemical catalysis of CO<sub>2</sub> reduction with organic metal modified electrodes is summarized by taking into account different functionalization methods.

