Abstract: Electrocatalytic CO₂ reduction to CO was achieved with a novel Mn complex, fac-[MnBr(4,4’-bispHosphonic acid)-2,2’-bipyridine](CO)₂ (MnP), immobilized on a mesoporous TiO₂ electrode. A benchmark turnover number of 112 ± 17 was attained with these TiO₂/MnP electrodes after 2 h electrolysis. Post-catalysis IR spectroscopy demonstrated that the molecular structure of the MnP catalyst was retained. UV/vis spectroscopy confirmed that an active Mn–Mn dimer was formed during catalysis on the TiO₂ electrode, showing the dynamic formation of a catalytically active dimer on an electrode surface. Finally, we combined the light-protected TiO₂/MnP cathode with a CdS-sensitized photoanode to enable solar-light-driven CO₂ reduction with the light-sensitive MnP catalyst.

The reduction of CO₂ to CO is viewed as a potentially lucrative and renewable source of a key chemical feedstock, as well as a strategy to reduce rising atmospheric CO₂ levels. Electrocatalysis by molecular transition-metal complexes is a viable means of achieving this transformation, typically offering excellent tunability[5] and selectivity[5] as well as providing opportunities to study the catalytic mechanism.[5] Alternatives based on inexpensive solid-state materials usually offer less well-defined catalytic centers that prevent a detailed understanding of the catalytic mechanism.[5]

Im mobilization of such molecular catalysts on electrode surfaces makes efficient use of the active metal centers and therefore enables a true appraisal of properties, such as the turnover number (TON).[5] However, in most cases reported to date, molecular catalysts were deposited on carbon[5a,5b] and Pt-based[5] electrodes. These offer low transparency to visible light, and only in very few cases have the surface-bound catalytic intermediates been characterized spectroscopically in situ.[5a,5b] Bimolecular reaction mechanisms, in which active dimers form during catalysis, have not been observed on electrode surfaces, and it has been thought that such mechanisms would be impeded by immobilization of a monomeric pre-catalyst.[5a,5b]

First-row transition-metal complexes based on [MnBr-(CO)₃(L)] (L = bipyridine and derivatives) have emerged in recent years as promising electrocatalysts for CO₂ reduction, owing to their high selectivity and low overpotential for catalysis.[5c,6] They also contain only Earth-abundant elements, which is a significant advantage over analogous Re-based catalysts.[5c,5d] The low overpotential is a direct consequence of the bimolecular reaction mechanism, whereby a Mn⁰—Mn⁰ dimer is formed after the first reduction of the homogeneous molecular catalyst, which then reduces CO₂ to CO (L = 4,4’-dimethyl-2,2’-bipyridine).[5c] However, the maximum TONS achieved by this class of complex for electrolytic CO₂ production are 34 after 18 h,[5b] and 36 after 6 h.[5c] Mn catalysts have been integrated onto electrodes in polymer films, such as Nafion, where they reached a TON of 14 based on the total amount of catalyst used.[5c] From electrochemical measurements it was proposed that the Mn⁰—Mn⁰ dimer forms in the polymer matrix, although this was not spectroscopically verified. Preliminary studies of an electro-polymerized pyrrole-based Mn catalyst deposited on silicon nanowires have also suggested photoelectrochemical (PEC) CO₂ reduction, based on cyclic voltammetry (CV) results.[5c]

Herein, we present a novel Mn⁰ CO₂ reduction electrocatalyst with a phosphonate functionality (MnP, Scheme 1) that allows anchoring and direct wiring between the catalytic center and a metal oxide surface,[5c] as has been achieved for an analogous phosphonate-modified Re complex.[5c] We employ a mesoporous TiO₂ electrode, because it offers 1) long-term stability and conductivity under reducing conditions,[5c] 2) a three-dimensional morphology for high cata-

Scheme 1. Schematic representation and proposed mechanism for CO₂ reduction by TiO₂/MnP (X = Br⁻ in the isolated compound).
lyst loading and to facilitate close inter-molecular interactions, and 3) transparency for spectroelectrochemical characterization of catalytic intermediates. The electrochemical investigations establish the heterogenized MnP as the best-performing Mn electrocatalyst to date, which was enabled by a dynamic TiO2|MnP interface and dimerization of the immobilized Mn catalyst. Finally, we present the first example of CO2 reduction by a Mn catalyst driven by full UV/Vis solar-spectrum irradiation, circumventing the typical instability of these compounds by combining the TiO2|MnP hybrid cathode in the dark with a CdS-sensitized photoanode.

MnP (Scheme 1) was synthesized by coordination of 4,4'-bis(phosphonic acid)-2,2'-bipyridine to pentacarbonyl manganese(I) bromide in ethanol under N2, while protected from light. The product was isolated as an orange solid in 63% yield and characterized by CHNP microanalysis, 31P-NMR spectroscopy, high-resolution mass spectrometry, and infrared (IR) spectroscopy (νCO = 2030, 1946, and 1930 cm⁻¹, Figure 1a), which confirmed a fac-Mn tricarbonyl species. Full synthetic and characterization details can be found in the Supporting Information. MnP was insoluble in CH2CN and therefore characterized by CV in DMF (Figure S1 in the Supporting Information). A catalytic wave at Eonset = −1.8 V versus Fc/F+ (Fc = [η-(C,H5)Fe]) was observed when H2O was added and the cell was purged with CO2. The presence of water in the electrolyte solution is known to significantly increase electrocatalytic CO2 reduction activity, by allowing the Mn–Mn dimer to directly react with CO2.[10a]

Mesoporous TiO2 electrodes were prepared by a doctor-blading procedure, applying a suspension of commercial P25 TiO2 nanoparticles (anatase/rutile (8/2) mixture, average particle size 21 nm) to a fluorine-doped tin oxide (FTO) coated glass electrode, and further experimental details can be found in the Supporting Information. Scanning electron microscopy (SEM) on the resultant electrode revealed a mesoporous film with a thickness of approximately 6 μm (Figure S2a). Loading of the catalyst onto the TiO2 electrode was achieved by drop-casting a methanol solution of MnP, resulting in 34 nmol Mn per cm² of geometrical surface area. The presence of IR bands at νCO = 2032 and 1928 cm⁻¹ in the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrum confirmed the presence of MnP on the electrode (TiO2|MnP; Figure 1a).

Immobilization and electronic communication of the MnP with a metal oxide was confirmed by adsorbing MnP on conducting and mesoporous tin-doped indium oxide (ITO) electrodes instead (film thickness approximately 7 μm, see Figure S2b and Supporting Information for experimental details). CV with ITO|MnP in anhydrous CH3CN (1.0 M Bu4NBF4) displayed a reversible wave at E = −1.6 V versus Fc+/Fc, assigned to the reduction of MnII to Mn0. The peak current was linearly dependent on the scan rate, indicative of an immobilized species in good electronic communication with the electrode (Figure S3).

TiO2 becomes conductive at potentials more negative than the conduction band (CB), thus the CV of TiO2|MnP can be employed to study electrocatalytic CO2 reduction. The CV scan of a bare (Mn-free) TiO2 electrode in CH3CN/H2O (19/1, 0.1 M Bu4NBF4) shows the filling and emptying of the conduction band of TiO2 (Figure 1b), as confirmed by the increase in absorbance in the λ = 600–850 nm region of the electronic spectrum at an applied potential, Eapp of −1.8 V versus Fc+/Fc (Figure S4).[19,20] Comparable CV features are observed with a bare TiO2 electrode under CO2 or TiO2|MnP under N2. However, TiO2|MnP purged with CO2 showed an increased current with an onset of E = −1.6 V versus Fc+/Fc, indicative of electrocatalytic CO2 reduction by the heterogenized MnP catalyst (Figure 1b). Furthermore, the ratio of cathodic to anodic charge in the forward and reverse CV scans increased from approximately 1:1 to 4:1 by changing TiO2 to TiO2|MnP under CO2, suggesting that conduction-band electrons of TiO2 are consumed by the Mn catalyst on the CV timescale and are therefore unavailable for discharging during the anodic scan.

The increased current arising from TiO2|MnP under CO2 was confirmed as being the result of the reduction of CO2 to CO by controlled-potential electrolysis (CPE). Figure 2a shows the gaseous products formed when TiO2|MnP electrodes were held at Eapp = −1.7 V versus Fc+/Fc in the dark under CO2, and monitored by gas chromatography (GC). After 2 h, an average of 1.10 ± 0.25% CO was produced, with the production of 3.75 ± 0.56 μmol CO, corresponding to a Faradaic efficiency (FE) of 67 ± 5%. The FE for H2 production was 12.4 ± 1.4%, and the formation of formate was not detectable by ion chromatography. The TONCO of 112 ± 17 was calculated based on the amount of MnP drop-cast onto the electrode, and is thus a lower limit since it assumes all MnP remains bound and active throughout CPE. This is the highest TONCO based on the total amount of catalyst used for a Mn catalyst in CO production, and was achieved at a low overpotential (η) of approximately 0.42 V, calculated using a standard potential for CO2 reduction to CO (E°(CO2/CO)) of −1.28 V versus Fc+/Fc in these conditions.[21] This is one of the lowest overpotentials observed for a transition-metal-based catalyst in non-aqueous solution.[14,22,23] The CO production was also matched only by a modified Fe-porphyrin in homogeneous DME solution (η = 0.41 V)[24] and a Mn catalyst that achieved a TONCO of 36 after 6 h (η = 0.35 V).[21]
TiO$_2$/MnP exhibited good CO selectivity, with a CO:H$_2$ ratio of approximately 12:1 after 1 h CPE, although this ratio was reduced to 5:1 after 2 h, presumably a result of desorption or degradation of the Mn catalyst during the second hour of electrolysis. In the absence of either CO$_2$ or the Mn catalyst (Figures S5a and S5b), no CO was produced. H$_2$ production by bare TiO$_2$ was 1.91 ± 0.31 μmol after 2 h, compared to 1.43 ± 0.22 μmol for TiO$_2$/MnP with a surface coverage of 22 nmol cm$^{-2}$ and 0.69 ± 0.08 μmol with a coverage of 34 nmol cm$^{-2}$ (see Figure 2a, Figure S5, and Table S1). Increasing amounts of MnP on TiO$_2$ therefore suppress H$_2$ in favor of CO production, suggesting that H$_2$ production by TiO$_2$/MnP may originate from unmodified areas of the TiO$_2$ rather than the catalyst itself.

IR and UV/Vis spectroscopies confirmed the molecular nature of MnP during catalysis on TiO$_2$. Figure 1a shows an ATR-FTIR spectrum of TiO$_2$/MnP taken after CPE for 20 min (Q = 0.37C, approximate TON$_{Mn}$ = 34), revealing peaks at $\tilde{\nu}_{CO} = 2042$ and 1943 cm$^{-1}$. These vibrational CO stretches closely match the spectrum of the as-prepared electrode, with a slight shift explained by exchange of coordinated Br$^-$ for a solvent molecule, and therefore demonstrate that the molecular structure of the catalyst remains largely unchanged during catalytic turnover. Deactivation of the Mn catalyst to a material that is no longer molecular would be unlikely to give high CO selectivity, corroborating Figure 2a.

The UV/Vis spectra of TiO$_2$/MnP before, during, and after 20 min CPE with $E_{app} = -1.7$ V versus Fc$/$/Fc are shown in Figure 2b. During CPE, bands at 630 and 820 nm were observed, which are assigned to the formation of an Mn–Mn dimer by comparison to similar peaks formed during homogeneous CPE of the unmodified [MnBr(bpy)(CO)$_3$]$_2$ (Table S2 for assignment) [25,26]. We excluded the formation of the mononuclear doubly reduced MnP anion, analogues of which are also known to reduce CO$_2$ when dimer formation is impeded, due to the lack of a strong peak at approximately 548 nm as found in an analogous Mn compound in THF (difference spectrum in Figure S6). After CPE for 20 min, the TiO$_2$/MnP was left under CO$_2$ without an applied potential, and the peaks resulting from the dimer were lost (Figure 2b). This was corroborated by the IR spectrum in Figure 1a, which indicated mainly the presence of the Mn$_2$ monomer, but with a small peak at 1865 cm$^{-1}$ and a broadening of the peak at 1943 cm$^{-1}$, assigned to a small amount of remaining dimer. These data are consistent with the mechanism shown in Scheme 1, with the formation of a steady-state concentration of the catalytically active Mn–Mn dimer. This intermediate then reacts with CO$_2$ before it can be identified ex situ, reforming the Mn$^+$ monomer as detected in the IR spectrum.

Immobilization of MnP on mesoporous TiO$_2$ creates a high local concentration of Mn$^+$ under reducing conditions at the electrode surface. Phosphonic acid modified molecules, such as MnP, display some lability when bound to TiO$_2$ [23] and phosphate buffer has been used to displace anchored catalysts from TiO$_2$ particles, demonstrating a dynamic interaction [24]. We propose that the high activity and low overpotential of this system is due to either temporary desorption of the catalyst, followed by dimerization and re-anchoring within mesoporous TiO$_2$, or the high local concentration of MnP placing the metal centers in an environment where they are predisposed to dimerization upon reduction.

Manganese carbonyl compounds, such as MnP, show instability under illumination [19] and tend to undergo photolysis and release CO ligands [25]. Consequently, the few reports of Mn-based CO$_2$ reduction photocatalysis use monochromatic or narrowly filtered light to prevent decomposition of the catalyst [14,24,26]. This photo-instability was observed for TiO$_2$/MnP, which displayed a significantly lower CO production of 0.39 ± 0.16 μmol (12 ± 3% FE) when CPE was performed under UV-filtered 1 sun illumination ($\lambda > 420$ nm to avoid TiO$_2$ band-gap excitation in this experiment) at $E = -1.7$ V versus Fc$/$/Fc for 2 h (Figure S7). The significant H$_2$ production (1.74 ± 0.6 μmol, 59 ± 8% FE) is consistent with degradation of MnP and possibly the formation of a catalytically active Mn deposit. Therefore, TiO$_2$/MnP cannot be used directly in a CO$_2$ reducing photocathode that efficiently absorbs sunlight and exposes the catalyst to irradiation.

An alternative strategy to drive CO$_2$ reduction using full solar-spectrum irradiation was implemented, integrating MnP into a photoelectrochemical circuit with a photocathode, wired to TiO$_2$/MnP, which was kept in the dark. CdS-sensitized ZnO nanosheet electrodes were prepared following a reported procedure (SEM in Figure S8a) [27] which absorb a broad spectrum of light below 530 nm according to the electronic spectrum shown in Figure S8b. These ZnO/CdS electrodes gave an anodic photocurrent in the presence of triethanolamine (TEOA) as a hole scavenger with an onset of $-1.65$ V versus Fc$/$/Fc, a potential at which TiO$_2$/MnP gives a cathodic current from CO$_2$ reduction (Figure 3a). The linear-sweep voltammetry (LSV) scan of a two-electrode, two-compartment PEC cell comprising a CdS/ZnO photoanode and a TiO$_2$/MnP cathode (kept in the dark) in Figure 3b shows a small photocurrent at zero bias, which
increased as a bias potential ($U_{\text{app}}$) was applied. To confirm that CO was produced, we performed CPE in a two-electrode configuration in CH$_3$CN/H$_2$O electrolyte solution (19/1, 0.1 M Bu$_4$NBF$_4$, 0.1 M TEOA, purged with CO$_2$). An applied potential of 0.6 V for 1 h passed a charge of 0.26 C, and 0.36 ± 0.07 mol of CO (26% FE, 2.6:1 CO$_2$:H$_2$ ratio, TON$_{CO}$ = 11. Figure S9) was measured. The lower CO production performance compared to the three-electrode electrocatalytic system could be due to the potentially disruptive presence of TEOA in the electrolyte solution, the lower charge passed and the different potential at the cathode. Nevertheless, this is the first example of full spectrum solar-light driven CO$_2$ reduction with a Mn catalyst.

In conclusion, we have presented MnP as a novel Mn-based CO$_2$ reduction catalyst that allows immobilization onto a mesoporous TiO$_2$ electrode with its phosphonic acid anchoring groups. The TiO$_2$|MnP cathode achieved efficient CO$_2$ reduction to CO, reaching an unprecedented TON$_{CO}$ of 112 ± 17 at an overpotential of 0.42 V after 2 h CPE. During electrocatalytic CO$_2$ reduction, a Mn–Mn dimer was formed, which is an important catalytic intermediate in homogeneous solution. This is, to our knowledge, the first observation of the dynamic formation of active catalytic dimers on a surface, providing a strategy for retaining homogeneous reaction mechanisms whilst also gaining the advantages of heterogeneous catalysis. Finally, we utilized the CO$_2$ reduction activity of TiO$_2$|MnP at a low overpotential to assemble a PEC cell with a CdS-sensitized photoanode, demonstrating that Mn catalysts can be used in solar-driven CO$_2$ reduction in spite of their photo-instability. This work represents an advance in moving molecular CO$_2$ reduction electrocatalysis towards a full artificial photosynthetic system. This was achieved through the immobilization of the catalyst, attainment of a high TON at low overpotential, and implementation of a PEC cell.

**Acknowledgements**

We gratefully acknowledge financial assistance from the EPSRC, the Christian Doppler Research Association (Australian Federal Ministry of Science, Research and Economy and National Foundation for Research, Technology and Development), and the OMV Group. We also thank Mr. Charles Creissen for performing SEM studies, and Dr. Moritz Kuehnel, Dr. Kristian Dalle, and Mr. Benjamin Martindale for helpful comments.

**Keywords:** carbon dioxide · electrocatalysis · hybrid materials · manganese · reduction

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**How to cite:** Angew. Chem. Int. Ed. 2016, 55, 7388–7392

**Angew. Chem. 2016, 128, 7514–7518**
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Received: January 29, 2016
Published online: April 25, 2016