

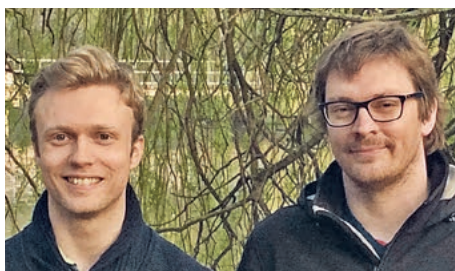
Heterogenised Molecular Catalysts for the Reduction of CO₂ to Fuels

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Abstract: CO₂ conversion provides a possible solution to curtail the growing CO₂ levels in our atmosphere and reduce dependence on fossil fuels. To this end, it is essential to develop efficient catalysts for the reduction of CO₂. The structure and activity of molecular CO₂ reduction catalysts can be tuned and they offer good selectivity with reasonable stability. Heterogenisation of these molecules reduces solvent restrictions, facilitates recyclability and can dramatically improve activity by preventing catalyst inactivation and perturbing the kinetics of intermediates. The nature and morphology of the solid-state material upon which the catalyst is immobilised can significantly influence the activity of the hybrid assembly. Although work in this area began forty years ago, it has only drawn substantial attention in recent years. This review article gives an overview of the historical development of the field.

Keywords: Catalysis · CO₂ reduction · Electrocatalysis · Heterogeneous · Photocatalysis



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Introduction

CO₂ capture and utilisation through chemical reduction has been a goal of chemists for many years.^[1] Interest in this process has intensified during the last decade to address concerns about global warming and dwindling reserves of accessible fossil fuels. Many catalysts are known to promote this process, including enzymes, solid-state materials and synthetic complexes.^[2] Enzymes operate very efficiently in terms of catalytic rate achieved per active site and limited energy loss, but are fragile and require specific operating conditions (close to ambient pH and temperature).^[3] Material-based systems often show high stability, but typically give poor selectivity as proton reduction is not suppressed and CO₂ conversion yields a range of different products.^[4] Synthetic molecular catalysts often show high selectivity with reasonable stability, and they are further tuneable through ligand design.^[2a] However, most molecular complexes currently only operate as homogenous catalysts in organic solvents, which prevents their use in aqueous solution and integration into devices.

Heterogenising molecular catalysts through immobilisation on solid-state supports has many potential benefits.^[5] The

catalyst no longer needs to be soluble in the reaction medium so a wider range of solvents is accessible. The catalyst can also be more easily separated from the reaction medium for recycling. Materials design can be exploited for the benefit of the catalytic system as a porous material can bind a large number of molecules due to the high surface area and can protect the catalyst to improve stability. CO₂ reduction requires electrons, which need to be delivered either by an electrode or a photoexcited light absorber. The photoexcited state lifetimes are typically faster than the diffusion limit with a dye and catalyst in solution. Subsequently, the catalyst struggles to collect the multiple electrons required in time to perform the desired reaction. Immobilising a catalyst on an electrode, light absorbing material or sensitised semiconductor pre-organises the electron donor (light absorber) and acceptor (catalyst), thus removing diffusional limitations and increasing the efficiency of the electron transfer. Immobilisation also prevents two catalyst cores diffusing together, suppressing deactivation through dimerisation. Thus, catalyst immobilisation appears to be a viable strategy for improving activity.

This review is divided into three sections: 1) electrocatalysis, 2) photocatalysis and 3) photoelectrocatalysis (Fig. 1).

1) Generally, any electrode will reduce CO₂ if a sufficiently negative potential is applied. However, the typical potential required will be far more negative than the thermodynamic potential and the product selectivity is expected to be poor. The additional bias is called the overpotential and

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can be thought of as the activation energy required to overcome the kinetic barrier of CO_2 conversion. When an electrocatalyst is added to the electrolyte solution, the overpotential is reduced. In heterogenised systems the molecular catalyst is bound to the electrode, usually by chemical or electrostatic interactions *via* an ‘anchoring group’ built into the molecule, or by polymerisation on the electrode surface (Fig. 1A). From a solar energy conversion perspective, these systems do not utilise solar light directly but could be powered by photovoltaics.

2) No electrode is required in photocatalysis and the energy for the reaction is obtained through light absorption. Electrons are typically supplied by a sacrificial reducing agent, although ultimately a more sustainable electron supply is needed. The system is constructed either with a molecule capable of both light absorption and catalytic CO_2 reduction (a photocatalyst) or by combining a light absorber (dye) with an electrocatalyst (Fig. 1B). Electron transfer from dye to catalyst is required and the lifetime of charge separation is critical. In heterogenised systems the electron transfer may also occur *through* the solid-state material. In some cases the material itself is the light absorber.

3) Photoelectrocatalysis eliminates the requirement of a sacrificial agent as the electrons are delivered from an electrode surface *via* an external circuit (Fig. 1C). Light is absorbed either by a semiconductor electrode or a co-immobilised molecular dye, and therefore some or all of the energy for the system is provided by sunlight.

The following main metrics will be used in this review to discuss the activity of CO_2 reduction catalysts. Turnover number, abbreviated to TON, is the ratio of the moles of product (denoted in subscript) to moles of catalyst. Faradaic efficiency, abbreviated to FE, only applies to electrocatalytic systems and is the fraction of electrons passed through the electric circuit to produce the desired product (denoted in subscript). For a quantitative FE in a two-electron process such as CO_2 reduction to CO or HCOOH, the number of electrons is twice the number of product molecules. The photocatalytic equivalent is the quantum yield, abbreviated to QY, which is the ratio of the moles of photons to moles of a product, corrected for the number of photons required to produce a specific product. The applied potential, given in volts, is a measure of the energy required to drive a specific redox reaction. The more positive the applied potential under comparable conditions, the smaller the energy loss in the system. In some cases, the overpotential is given. Herein, for comparison, all electrode potentials are given *vs* the normal hydrogen electrode (NHE).^[6]

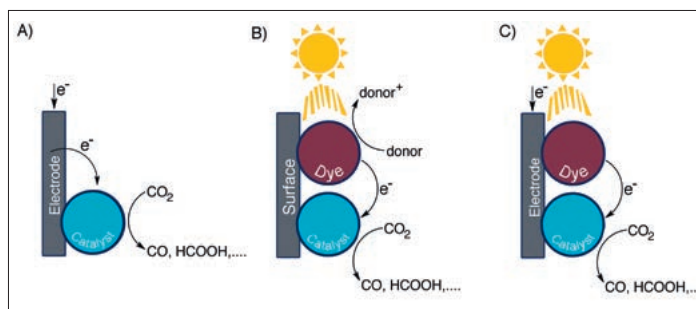


Fig. 1. Schematic diagrams of heterogeneous molecular systems for: A) electrocatalysis, B) photocatalysis and C) photoelectrocatalysis.

Electrocatalytic CO_2 Reduction

The earliest example of an immobilised molecular catalyst for CO_2 reduction comes from work by Meshitsuka, Ichikawa and Tamaru in 1974.^[7] Graphite electrodes were immersed in suspensions of a range of metal phthalocyanines in benzene, allowed to dry and analysed in an aqueous electrolyte solution. Phthalocyanines are good candidates for immobilisation due to their poor solubility in common solvents and their planar aromatic structure allows for π - π stacking with graphite. The Co and Ni phthalocyanines displayed good electrocatalytic currents under CO_2 compared with N_2 and oxalic and glycolic acids were qualitatively detected. Lieber and Lewis reported more quantitative measurements of immobilised Co phthalocyanine in 1984.^[8] Deposited onto a carbon cloth from THF, the catalyst showed excellent selectivity for the production of CO at an overpotential of 300 mV in pH 5 citrate buffer. The system yielded a $\text{TON}_{\text{CO}} = 10^5$ at a turnover frequency (TOF_{CO}) of 100 s^{-1} . Homogeneous Co phthalocyanine produced only $\text{TON}_{\text{CO}} = 4$ and it was suggested that this is due to unfavourable interactions between catalyst sites, which are suppressed when the catalyst is immobilised.

In 1991 Enyo *et al.* functionalised a glassy carbon electrode with pyridine coordinated to Co tetraphenyl porphyrin. First, the electrode was anodised to produce surface-exposed carboxylate groups, followed by refluxing in thionyl chloride and exposing the electrode to 4-aminopyridine to form an amide bond between the pyridine and carbon surface.^[9] The anchored pyridine was then coordinated to the axial position of Co tetraphenyl porphyrin (CoTPP; Fig. 2A). Electrocatalytic CO_2 reduction was observed in pH 7 phosphate buffer with an overpotential of 300 mV. The electrode displayed excellent selectivity and stability with $\text{FE}_{\text{CO}} = 92\%$ and $\text{TON}_{\text{CO}} = 10^7$. H_2 generation was observed in the absence of CO_2 . Homogeneous CoTPP in DMF showed poor stability and activity ($\text{TON}_{\text{HCOOH}} < 50$), producing formate with $\text{FE}_{\text{HCOOH}} = 10\%$ and the catalytic activity was not enhanced upon addition of pyridine. It was suggested that immobili-

sation isolates the Co centres from one-another preventing them from interacting, and that pyridine increases the electron donating ability of the Co.

In 1988 Abruña and colleagues reported the immobilisation of a Co terpyridine (tpy) catalyst for CO_2 reduction to CO.^[10] A vinyl-functionalised tpy complex was

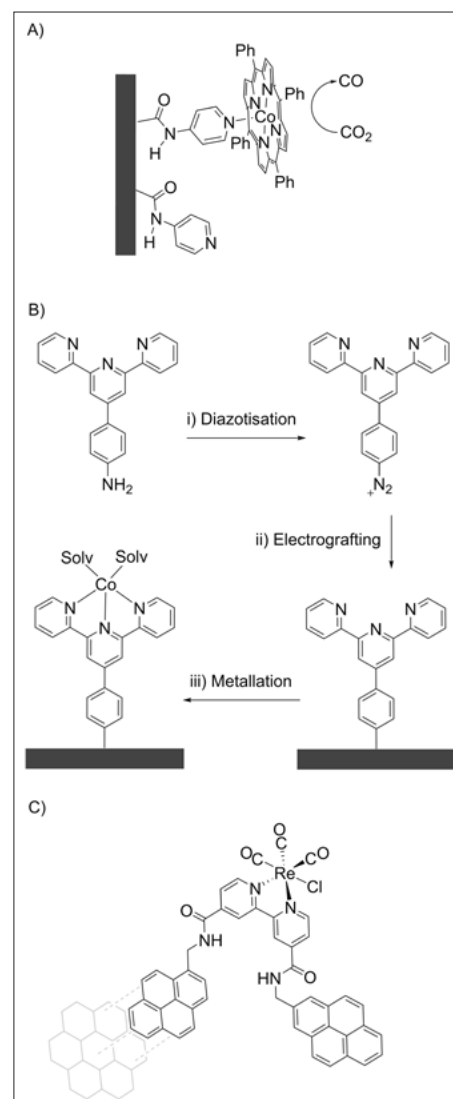


Fig. 2. A) Co tetraphenyl porphyrin co-ordinated to pyridine grafted onto a glassy carbon electrode.^[9] B) A diazonium functionality allows *in situ* grafting of a tpy ligand to the glassy carbon electrode surface.^[12] C) $[\text{ReCl}(\text{bpy})(\text{CO})_2]$ catalyst functionalised with pyrene units in the 4,4' position of the bpy ligand for π - π stacking on carbon electrodes.^[17]

electro-polymerised on Pt electrodes and in dimethyl formamide (DMF) showed catalytic currents at 860 mV less negative potential than homogeneous $[\text{Co}(\text{tpy})_2]^{2+}$. In 1993 Kaneko and co-workers followed this up and studied $[\text{Co}(\text{tpy})_2]^{2+}$ immobilised in a Nafion membrane on carbon electrodes in aqueous electrolyte solution.^[11] At -0.85 V vs NHE in pH 7 phosphate solution, $\text{FE}_{\text{HCOOH}} = 51\%$ and $\text{FE}_{\text{H}_2} = 13\%$ was observed with a low $\text{TON}_{\text{HCOOH}} = 11$. In 2015 Fontecave and colleagues functionalised a carbon electrode with terpyridine through diazonium coupling (Fig. 2B).^[12] The terpyridine was subsequently metalated with Co upon immersion in a solution of CoCl_2 in DMF. Electrolysis in DMF under a CO_2 atmosphere at a very negative potential (-1.73 V vs NHE) gave $\text{TON}_{\text{CO}} = 70$. In the absence of CO_2 in either DMF or phosphate buffer, H_2 was produced.

In 1983 Lehn and co-workers reported that $[\text{ReX}(\text{bpy})(\text{CO})_3]$ ($\text{bpy} = 2,2'$ -bipyridine; $\text{X} = \text{Cl}^-$ or Br^-) complexes are selective photocatalysts for CO_2 reduction to CO (see more detailed discussion below).^[13] In 1984, they demonstrated the electrocatalytic activity of the same complexes,^[14] and in 1985 Meyer and colleagues reported on the heterogenisation of this catalyst by electro-polymerising $[\text{ReCl}(\text{CO})_3(4\text{-vinyl-4'-methyl-2,2'-bipyridine})]$ onto Pt electrodes.^[15] Electronic absorption spectroscopy and X-ray photoelectron spectroscopy prior to catalysis indicated that the molecular structure was retained on the electrode. At an applied bias of -1.30 V vs NHE in CH_3CN , the Re-modified electrode showed good selectivity and electrocatalytic activity for the production of CO with $\text{FE}_{\text{CO}} = 92\%$ and $\text{TON}_{\text{CO}} = 516$. Cyclic voltammetry (CV) after 80 min showed that the electroactive Re catalyst had been lost from the surface. The Re catalyst monomer showed a $\text{TON}_{\text{CO}} = 30$ in homogeneous catalysis under comparable conditions and it was suggested that polymerisation favours an alternative more reactive pathway and stabilises the catalyst to decomposition.

Kaneko and co-workers studied immobilised $[\text{ReBr}(\text{bpy})(\text{CO})_3]$ on graphite electrodes by casting a DMF/alcohol solution of the catalyst mixed with Nafion onto the surface of basal plane graphite.^[16] Electrolysis in pH 7 phosphate solution showed CO_2 reduction to a range of products, and the product distribution was dependent on the applied potential. $\text{FE}_{\text{CO}} = 29$, $\text{FE}_{\text{HCOOH}} = 48$ with $\text{TON}_{\text{CO}} = 198$, $\text{TON}_{\text{HCOOH}} = 148$ were obtained under optimised conditions (between -1.05 and -1.35 V vs NHE) with the major side product being H_2 . Homogeneous $[\text{ReBr}(\text{bpy})(\text{CO})_3]$ was less active, giving $\text{TON}_{\text{CO}} = 21$ after one hour compared with 166 after one hour for the heterogenised cat-

alyst. However, care must be taken when comparing TONs between homogeneous and heterogeneous systems. In a homogeneous system, only a small fraction of the dissolved catalysts is turning over at the electrode surface, whereas all of the heterogenised catalysts can in principle operate. TONs taken before inactivation of the system can result in a drastic underestimate of the bulk activity. More recently Brunshwig, Gray and co-workers functionalised a $[\text{ReCl}(\text{bpy})(\text{CO})_3]$ catalyst with pyrene groups for immobilisation on graphite electrodes through π - π stacking (Fig. 2C).^[17] At a rather negative applied potential of -1.67 V vs NHE in CH_3CN , $\text{FE}_{\text{CO}} = 70\%$ and $\text{TON}_{\text{CO}} = 58$ were obtained and the catalyst had lost activity after 1 h of electrolysis.

In 2011 it was reported that Mn analogues of the well-established $[\text{ReX}(\text{bpy})(\text{CO})_3]$ ($\text{L} = \text{Br}^-$, CH_3CN) catalysts are active for electrocatalytic CO_2 reduction.^[18] This is important from a scale-up perspective as Mn is 1.3 million times more abundant than Re in the Earth's crust.^[19] The Mn catalyst operates at a lower overpotential relative to the Re analogue.^[18] Cowan and colleagues immobilised $[\text{MnBr}(\text{bpy})(\text{CO})_3]$ in a Nafion membrane onto a glassy carbon electrode and produced CO and H_2 in a ratio of 1:2 at -1.17 V vs NHE in pH 7 phosphate solution.^[20] Addition of multi-walled carbon nanotubes increased the number of electro-active molecules in the membrane from 0.25% to 11%. The Nafion immobilised system produced CO at 100 mV less negative potentials than for homogeneous $[\text{MnBr}(\text{bpy})(\text{CO})_3]$ (in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$). This example highlights how immobilisation can affect energy requirements and therefore the efficiency of the system.

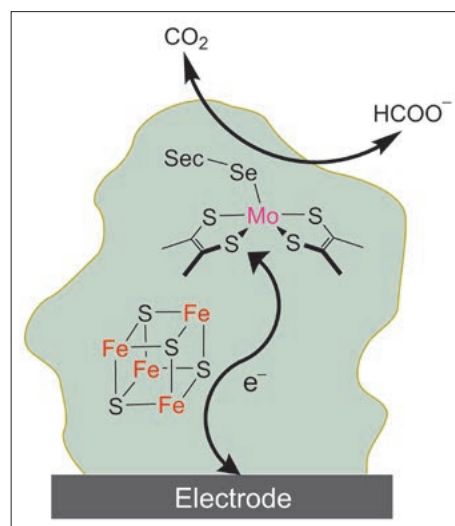


Fig. 3. Formate dehydrogenase on a carbon/epoxy electrode interconverts CO_2 and formate reversibly. Electrons are transferred to the Mo active site via an iron sulphur cluster.^[20a]

Other CO_2 reduction systems include those using enzymes. Protein film electrochemical studies of a molybdenum- and tungsten-containing formate dehydrogenase have shown that this class of enzyme can reversibly inter-convert CO_2 and formate at the thermodynamic potential (*i.e.* in either direction with minimal overpotential) and with quantitative FE and selectivity (Fig. 3).^[3a,21] Reversibility has also been demonstrated with a nickel/iron-containing carbon monoxide dehydrogenase.^[22]

Photocatalytic CO_2 Reduction

Photocatalytic CO_2 reduction cuts out the electrolytic middleman in solar fuels synthesis. Instead of relying on a photovoltaic panel for providing the electricity to drive electrolysis, photocatalysis involves the direct conversion of light into a CO_2 reduction product. Generally, there are two options to promote the photocatalytic reaction. (1) A photocatalyst acts as both light absorber and CO_2 reduction catalyst, or (2) a light absorbing molecule (dye) or semiconductor is used to sensitise a CO_2 reduction electrocatalyst. There are very few examples of system (1)^[13,23] with Lehn's $[\text{ReX}(\text{bpy})(\text{CO})_3]$ -type catalyst ($\text{X} = \text{Cl}^-$, Br^-) being the best known and studied. Examples of system (2) are more common and a range of catalyst and dye combinations have been reported.^[24] Photocatalytic reactions do not involve electrical wiring to reduce the oxidised dye or photocatalyst, and a chemical reductant is required to allow for catalytic turn over. Typical reductants are triethanolamine (TEOA), Et_3N and ascorbic acid, which are consumed during the reaction and are therefore termed 'sacrificial electron donors'. The eventual goal is to replace these donors with a sustainable source of electrons such as water.

The first example of a heterogenised molecular CO_2 reduction photocatalyst comes from Ramaraj and Premkumar in 1997.^[25] Metal phthalocyanines and porphyrins were adsorbed into a Nafion membrane and irradiated with visible light in HClO_4 solution with Et_3N as electron donor. Co tetraphenylporphyrin showed excellent activity and stability, giving a $\text{TON}_{\text{HCOOH}} = 1.7 \times 10^4$. Protoporphyrin, Fe phthalocyanine and Zn phthalocyanine also showed respectable photo-activity.

In 2013 Ishitani and colleagues immobilised a dyad, consisting of a $[\text{Ru}(\text{bpy})_3]^{2+}$ dye covalently linked to a catalytic $[\text{RuCl}_2(\text{bpy})(\text{CO})_2]$ unit, onto Ag-modified TaON particles via phosphonate anchoring groups (Fig. 4A). The photo-generated hole in the valence band of the TaON, with the Ag co-catalyst, oxidises MeOH to formaldehyde and the conduction band electrons reduce an excited or oxidised $[\text{Ru}(\text{bpy})_3]^{2+}$

unit.^[26] This tandem process allows for the coupling of CO₂ reduction with the oxidation of MeOH to formaldehyde instead of radical decomposition of amines through oxidation. Visible light irradiation ($\lambda > 400$ nm) in MeOH produced $\text{TON}_{\text{HCOOH}} = 41$, along with significant quantities of H₂ and a small amount of CO. The total moles of reduction products was equal to the moles of HCHO produced. Isotope labelling studies demonstrated that the HCOOH carbon atom originated from CO₂ and the HCHO carbon came from MeOH.

In 2015 Ishitani, Maeda and colleagues reported a Ru complex with phosphonate groups adsorbed on carbon nitride (C₃N₄), an organic polymer with semiconductor properties (Fig. 4B).^[27] C₃N₄ is currently receiving attention because of its stability and response to visible light.^[28] The Ru catalysts were active on C₃N₄, producing HCOOH and small amounts of H₂ and CO. The most active was a Ru catalyst without methylene spacers between the bpy and phosphonic acid groups (Fig. 4B). This system displayed good stability, efficiency and selectivity with C₃N₄ when using dimethylacetamide (DMA) as a solvent, 20% TEOA electron donor and $\lambda > 400$ nm. The system produced $\text{TON}_{\text{HCOOH}} = 1000$ (over 20 h) with a QY of 5.7% ($\lambda = 400$ nm).^[27]

Recently, Fontecave and co-workers functionalised a Rh CO₂ reduction catalyst with two carboxylic acid groups for incorporation into a metal organic framework (MOF). The catalyst, Cp*Rh(bpydc)Cl₂ (bpydc = 2,2'-bipyridine-5,5'-dicarboxylic acid) was inserted into a MOF with the formula Zr₆(OH)₄(O)₄(biphenyl-4,4'-dicarboxylate)₆.^[29] Post functionalisation exchanged some of the biphenyl-4,4'-dicarboxylate units for the Rh catalyst containing the 2,2'-bpy-5,5'-dicarboxylic acid ligand. A photocatalytic system with the MOF loaded with 10% Rh catalyst and [Ru(bpy)₃]Cl₂ as dye in CH₃CN/TEOA 5:1 produced a $\text{TON}_{\text{HCOOH}} = 47$ and $\text{TON}_{\text{H}_2} = 36$, but comparable results were also obtained with the free Rh catalyst in the absence of the MOF ($\text{TON}_{\text{HCOOH}} = 42$ and $\text{TON}_{\text{H}_2} = 38$). Increasing loadings of the Rh catalyst in the MOF drastically reduced HCOOH production and increased H₂ production. It is suggested that the system thermally dehydrogenated HCOOH at higher catalyst loadings to produce H₂ and CO₂. Increasing the amount of catalyst in the homogeneous system simply led to deactivation, with virtually no HCOOH or H₂ produced. The heterogeneous MOF system could be recycled up to six times or after four days of cumulative photolysis.

Kang and co-workers reported a system comprising a [ReCl(bpy)(CO)₃] type catalyst and an organic dye co-adsorbed onto TiO₂ nanoparticles.^[30] The bpy of

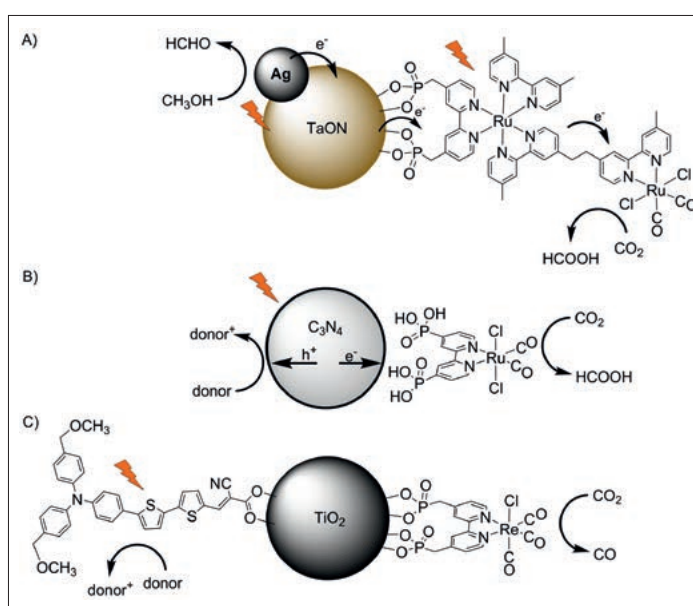


Fig. 4. Photocatalytic CO₂ reduction systems A) Tandem CH₃OH oxidation and CO₂ reduction by Ag and Ru complex, respectively. [Ru(bpy)₃]²⁺ derivative and TaON are light absorbers.^[26] B) Ru catalyst on visible light absorbing C₃N₄.^[27] C) Re catalyst and organic dye on TiO₂.^[30]

the Re catalyst had phosphonate anchors at the 4 and 4' positions, with a methylene group between the bpy and phosphonate, whereas the dye had one carboxylate anchoring group (Fig. 4C). A range of TiO₂ sources were tested and the highest activity (TON_{CO} up to 435) came from TiO₂ with an anatase nanosheet morphology (20 nm length \times 5 nm thick). This example highlights the importance of engineering the surface to which the catalyst is immobilised. The loading order of dye and catalyst was investigated and if the dye was adsorbed first, an additional 40 TON_{CO} was observed in some cases, compared with absorbing the catalyst first. This is likely to be because the catalyst is binding much more strongly due to the two phosphonate anchoring groups and is covering much of the TiO₂ surface before the dye can access it. Catalytic testing was in the typical DMF solvent but with an atypical electron donor, 2-phenyl benzoimidazole at 0.1 M. Irradiation of $\lambda > 420$ nm was employed, which could lead to direct excitation of the Re catalyst as well as the dye. In contrast with previous reports for CO₂ reduction by Re catalysts,^[24a,31] addition of 10% water enhanced activity but addition of TEOA reduced activity. Despite the semiconducting nature of TiO₂, a through-particle electron transfer is unlikely because of the mismatch in the relevant electrochemical potentials of the photo-excited dye, TiO₂ and catalyst.

Work in our group has focused on the use of phosphonate anchoring groups to bind molecules tightly to the surface of metal oxide nanoparticles, in particular TiO₂. Phosphonate anchoring groups are a good candidate because their binding constants for TiO₂ are typically an order of magnitude greater than that of carboxylate groups and they are much less sensitive to water and less acidic conditions.^[32] There

are several examples where separate dye and catalyst molecules have been immobilised on TiO₂ that catalytically reduce H⁺ to H₂ with visible light.^[33] TiO₂ nanoparticles were chosen to provide long-lived charge separation. The dye can inject electrons into the conduction band of the TiO₂, which subsequently transfers electrons to the catalyst (Fig. 5A). It was demonstrated that the conduction band electrons have a lifetime up to 0.8 s.^[34]

We recently reported a system in which a [ReL(bpy)(CO)₃] (L = 3-picoline or Br⁻) photocatalyst was modified with phosphonate anchors and thus bound to TiO₂ nanoparticles (Fig. 5B).^[35] The molecule was intact on the TiO₂ surface and displayed strong performance. Previous reports of heterogenised [ReCl(bpy)(CO)₃] had shown the immobilised complex to be significantly less efficient as a photocatalyst than comparable homogeneous systems, $\text{TON}_{\text{CO}} = 7$ vs $\text{TON}_{\text{CO}} = 30$ for homogeneous [ReCl(bpy)(CO)₃].^[36] This was in accord with other work showing that structural changes made to the bpy ligand result in a reduction of TON_{CO} .^[31] We showed that a [ReL(CO)₃] unit (L = 3-picoline, Br⁻) coordinated to a bpy ligand with phosphonate groups in the 4- and 4'-position ('ReP') bound tightly to TiO₂. ReP-TiO₂ significantly outperformed homogenous ReP, which was essentially inactive under comparable conditions. ReP-TiO₂ ($\text{TON}_{\text{CO}} = 52$) also performed better than the homogeneous benchmark photocatalyst [ReCl(bpy)(CO)₃] ($\text{TON}_{\text{CO}} = 30$). Transient absorption spectroscopy measurements were performed on ReP in solution and adsorbed onto TiO₂. The Re photocatalyst was excited with visible light to produce an MLCT excited state. Reductive quenching by the electron donor, TEOA reduces the catalyst, which subsequently reacts with CO₂. The reduced ReP intermediate had a

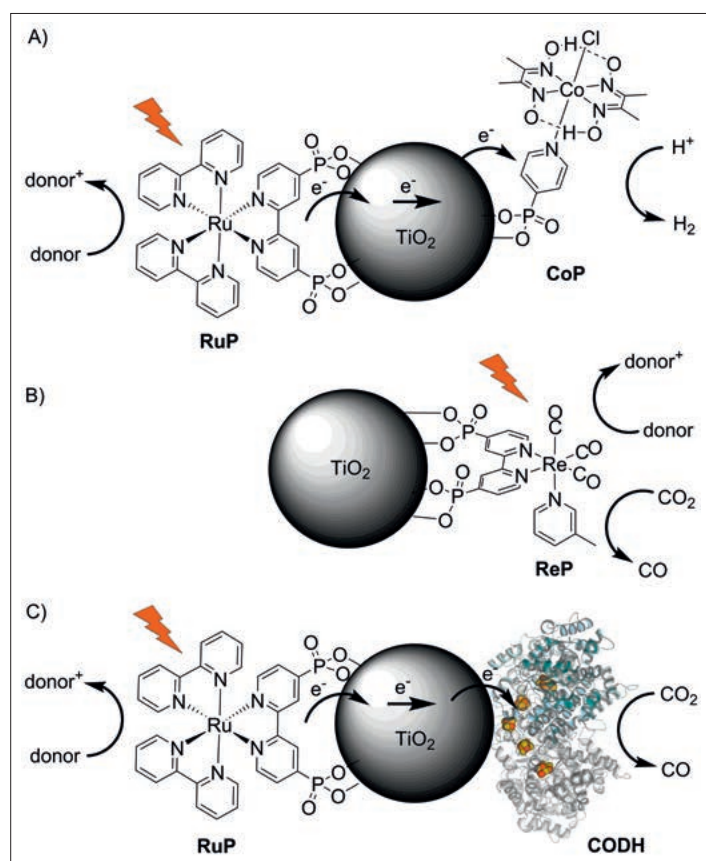


Fig. 5. A) Dye (RuP) and proton reduction catalyst (CoP) co-loaded onto TiO_2 nanoparticles.^[39] B) Re photocatalyst on TiO_2 .^[35] C) CO_2 reduction by carbon monoxide dehydrogenase with RuP as light absorber on TiO_2 .^[37]

lifetime one order of magnitude greater on TiO_2 than in homogeneous solution. There was also evidence of reduced dimerisation of the catalyst when bound to the TiO_2 surface. Signals in the near-IR region of the spectrum, assignable to Re-dimers, were smaller in amplitude for the ReP- TiO_2 system relative to ReP.

In an effort to make solar-powered enzymes, Armstrong and co-workers immobilised a carbon monoxide dehydrogenase onto dye-sensitized TiO_2 .^[37] This is a viable strategy for photosensitising an enzyme and achieving charge separation, where covalent attachment of a dye would be very challenging. The system produced CO at a turnover rate of 0.15 s^{-1} (Fig. 5C). The activity decreased significantly during the first four hours of operation, indicating the fragility of the employed enzyme. A related hydrogenase-based system reduced protons to H_2 at a turnover rate of 50 s^{-1} .^[38]

Photoelectrocatalytic CO_2 Reduction

Photoelectrocatalysis can combine the benefits of photocatalysis and electrolysis. A catalyst may be combined with a light-adsorbing electrode, or a dye and catalyst are co-adsorbed on an electrode. In this case, the driving force for the chemical reaction is obtained through light absorption and the electrons are delivered from an anode, where a sustainable oxidation re-

action can occur, such as water oxidation. Thus, no (or only a small) electrochemical potential is required to perform the reduction of CO_2 at the cathode.

Photoelectrocatalytic CO_2 reduction can be achieved through layer-by-layer assembly: integrating a CO_2 reduction catalyst on top of a dye, which is adsorbed on a p-type semiconductor is a viable strategy. In this scenario, the dye layer absorbs visible light and the electrons are transferred to the catalyst. The oxidised dye is subsequently re-generated by hole transfer to the semiconductor, resulting in a cathodic current from CO_2 reduction. The dye layer may be molecular or a semiconducting material.

In 1986 Abruña and colleagues reported a polymer film of $[\text{ReCl}(4\text{-vinyl-4'-methyl-2,2'-bipyridine})(\text{CO})_3]$ on two types of light-absorbing electrodes, p-Si and polycrystalline p-WSe₂.^[40] Immobilisation was achieved by cycling the electrode potential in an acetonitrile electrolyte solution of the Re complex. UV-vis spectra of the polymer showed monomeric and dimeric Re centres. For both photoelectrode materials the potential required for the onset of catalytic CO_2 reduction was reduced by 150 mV when illuminated and a TON_{CO} of the order of 450 was observed. The FE_{CO} for the p-Si electrode was unity. Assuming the He/Ne laser used was emitting at 633 nm, excitation of the dimeric Re centres (λ_{max} approximately 600 nm) cannot be ruled out.

Perhaps the most impressive example

of photoelectrocatalytic CO_2 reduction to date came from Sato, Arai and colleagues in 2011.^[41] A mixture of Ru complexes immobilized on an InP photoanode was coupled to a Pt- TiO_2 photoanode capable of water oxidation. The TiO_2 anode absorbs UV light and the InP harvests the longer wavelength visible light (Fig. 6A). The system was able to photocatalytically reduce CO_2 to formate ($\text{TON}_{\text{HCOOH}} > 17$) with *no external bias* and with electrons derived from photocatalytic water oxidation at the anode. The Faradaic efficiency for formate was 70% with some CO and H_2 produced as by-products. Critically, isotopic labelling demonstrated that the carbon and protons in the formate were derived from CO_2 and H_2O respectively, and that O_2 came from H_2O oxidation. The system operates in an aqueous electrolyte solution and with sunlight. This work demonstrates the principle of tandem CO_2 reduction and H_2O oxidation *via* photoelectrocatalysis using just solar energy.

In 2014 Inoue and co-workers reported photoelectrocatalytic CO_2 reduction with a molecular dyad.^[42] A zinc porphyrin dye was covalently attached to a Re catalyst. A carboxylate group on the zinc porphyrin anchored the dyad onto p-type NiO electrodes (Fig. 6B). In DMF the system produced CO catalytically with no H_2 detected. The Faradaic efficiency for CO was 6.2% and $\text{TON}_{\text{CO}} = 10$ over 50 h. Co-adsorbing an additional zinc porphyrin dye improved the TON_{CO} by an order of magnitude but caused a four-fold drop in the Faradaic efficiency for CO. The authors suggest that the low efficiency is in part due to the dyad requiring two electron transfers from porphyrin to Re in order to reduce CO_2 . A comparable system, where the catalyst was not immobilised, showed $\text{FE}_{\text{CO}} = 13\%$ because two one-electron reduced catalysts can come together to accumulate the two electrons for CO_2 reduction.

Other Chemical Reactions Catalysed by Heterogenised Compounds

The heterogenisation of molecular catalysts holds great promise for many other chemical reactions. There is also much work and scope for related systems of proton reduction^[33,43] and water oxidation.^[44] Aside from solar fuel reactions, the heterogenisation of alkene metathesis catalysts has received much attention.^[45] Tungsten alkylidene complexes were anchored onto partially hydroxylated Si. In several cases, the heterogeneous system significantly outperformed the homogeneous system.^[46] In one example, homogeneous precursors were essentially inactive for the homocou-

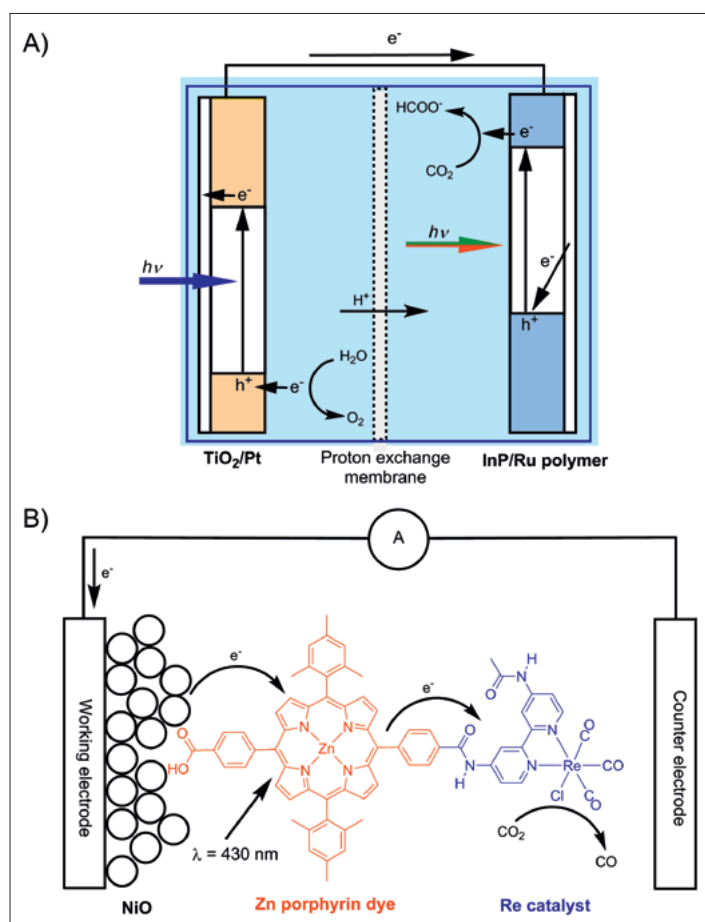


Fig. 6. A) Schematic representation of the cell for tandem photoelectrocatalytic CO₂ reduction and water oxidation.^[41] B) Zinc porphyrin Re complex dyad absorbed on a NiO electrode.^[42]

reduction catalysis. New homogeneous molecular catalysts are frequently reported and are immediate candidates for heterogenisation. There is room for development of the surfaces to which the molecules are attached and new anchoring strategies are being developed as well.^[32,48] The electronics of semiconducting surfaces can be varied for efficient light harvesting and/or electron transfer. The geometry and porosity of the surfaces will also play an important role. Advances to come are likely to involve the development of surfaces decorated with non-innocent chemical groups. Such a strategy may promote catalysis by creating a chemical environment around the molecule, mimicking the protein environment around an enzyme active site.

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pling of *cis*-4-nonene whereas the heterogeneous systems were capable of up to 138 turnover numbers per minute.^[47]

Conclusions and Outlook

Heterogenisation of molecular catalysts is a promising approach to establish more effective catalytic CO₂ conversion systems. Pioneering work showed already in 1974 that heterogenisation of a Co phthalocyanine resulted in a 25,000-fold enhanced activity compared to the corresponding homogenous system.^[8] Activity in this field is now growing quickly and this is a reflection of the overall renewed interest in artificial photosynthesis.

Heterogenisation brings together advantages from homogenous and heterogeneous catalysis. Products can be easily separated and limitations from solubility of a homogenous catalyst can be avoided. The immobilisation of catalysts can also prevent the formation of inactive species through dimerisation and thereby enhance the activity and stability of the catalytic system.^[8,35,45c] Recent findings demonstrate that immobilisation can alter the kinetics of photo-generated catalytic intermediates to improve the system's activity.^[35] Co-assembly of catalysts and dyes onto semiconductor surfaces provides pre-organisation, overcoming diffusional limi-

tations, which is important in light-driven systems. Furthermore, these materials can be non-innocent, in some cases providing long-lived charge separation *via* electron transfer into the conduction band,^[39] thereby promoting the activity and longevity of the system. In other cases the material itself is the light absorber allowing for efficient electron transfer to an immobilised catalyst.

In electrochemical systems, catalyst immobilisation prevents short-circuiting due to diffusion of the reduced catalytic intermediates to the counter electrode. There are also benefits in terms of measuring electrochemical systems. Turnover numbers and turnover frequencies can be more meaningfully determined when the catalyst is immobilised. Immobilisation of molecular catalysts also makes more efficient use of the individual catalytic centres, as opposed to homogeneous electrocatalysis, where the vast majority of molecules are in the bulk solution. The use of porous electrode materials can significantly increase the surface area and therefore increases the current density for optimal electrocatalytic performance. Immobilisation has led to a reduction in overpotential compared with homogeneous counterparts,^[20] and has allowed catalysis to move into aqueous solvent.^[16]

The future is likely to hold many more advances in heterogenised molecular CO₂

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