
Hybrid materials for electrocatalysis and photoelectrocatalysis

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Hybrid materials are materials composed of different classes of materials forged into one for a particular application. These materials are often a combination of both organic and inorganic/metallic constituents. In both electrochemical and photoelectrochemical processes, hybrids have been applied in the splitting of water as well as the conversion of nitrogen to ammonia amongst others. And while they have often been reported to function better than catalysts derived from single atoms, the manner in which hybrids operate as catalysts remains a grey area as there are limited accounts outlining the contribution made by each component of the whole entity. This chapter provides some insight on hybrid materials and their classifications, their syntheses and applications as electrochemical and photoelectrochemical catalysts, and how their catalytic abilities cannot always be reduced to the concept of synergy.

1 Introduction

Catalysis is described as the acceleration of a chemical reaction through the application of a catalyst. Catalysts achieve this feat by lowering the activation energy required to initiate the reaction.¹ The classification of catalysis consists of three categories, homogeneous, heterogeneous and, autocatalysis.^{1,2} In homogeneous catalysis, the catalyst exists in the same phase of matter as the reactants whereas with heterogeneous catalysis, the catalyst assumes a different state of matter from the reactants.^{1,2} In the case of an autocatalyst, there is no addition of an actual catalyst but one of the products functions as a catalyst to the same reaction from which it is generated. Generally, catalysts can exist as either a gas, solid or a liquid.¹

In electrochemistry, which is a field of study concerned with the movement of electrons and ions, catalysts are used to modify electrode surfaces. The combination of catalysis and electrochemistry is known as electrocatalysis and in this area of study, heterogeneous catalysis is preferred over homogeneous catalysis as the field is concerned primarily with the development and assessment of electrocatalysts on the electrode surface.^{1,3} A general scheme of an electrochemical cell is shown in Fig. 1 illustrating a cell's primary components, the anode and the cathode as well as the electrolyte.

More recently, developments in improving electrocatalytic systems have been made through the inclusion of light. The combination of electrocatalysis and photocatalysis has yielded a new form of catalysis known as photoelectrocatalysis (PEC).^{4,5} Photoelectrocatalysis incorporates both photoelectrons and electron holes to enable the initiation of reactions that are considered thermodynamically unfavourable through supplying the system with energy from an external source.^{5,6}

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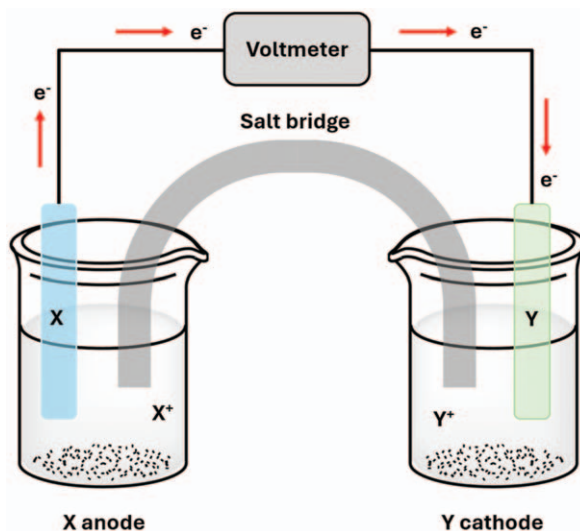


Fig. 1 Schematic diagram illustrating the basic components of an electrochemical cell.

The gradual merging of catalytic processes has been a major propellant in the design and fabrication of hybrid materials. With the development of these hybrid materials, there has been a surge in multi-atom catalysts and a significant change in the preferred sizes with nanosized catalysts receiving greater traction than their micro-sized counterparts.^{7–9} The reasons for the aforementioned are based on the fact that hybrid materials are derived from different materials *i.e.* organic, inorganic and/or metallic and that nanosized materials have been noted to exhibit intrinsic properties that are not observable in their bulk counterparts.^{10,11} The next section provides a detailed discussion on hybrid materials and their various classifications/categories.

2 Hybrid materials and their classifications

Hybrid materials are materials derived from two or more substances of a different composition at a molecular or nanometer level.¹² According to Yamamoto and colleagues, a hybrid is the result of a covalent or any other bond forming between different materials. Although classification is often based on the type of bond that exists between the two materials, size is also considered as a determinant in the construction of categories.¹³ Similar to Yamamoto, Makishima also based their categorization on chemical-bond modes which gave rise to four categories, namely: composites, nanocomposites, hybrids and nanohybrids. Composites are described as mixtures composed of matrices and dispersions at the micron level with nanocomposites being of a similar composition but existing below the micron level.¹³ Hybrids on the other hand, are defined as mixtures at the sub-micron level composed of varying materials with nanohybrids being mixtures of the same kind at the atomic level in which the various components are bound to each other through chemical bonds. The distinction between composites/nanocomposites and

hybrids/nanohybrids is that the pool of materials for hybrids is greater than that associated with composites.^{12,13}

The consensus as far as defining hybrid materials is concerned has been confined primarily to the notion that these materials are composed of both organic and inorganic materials. Gómez-Romero and Sanchez, a pair that was not adamant on the existence of chemical bonds, placed greater emphasis on size with their classification of hybrids excluding materials larger than 100 nm in size.¹³ This received a great deal of support from The Materials Science Society of Japan as marked by their publication in 1993.¹⁴ According to The Materials Science Society of Japan, hybrids are a nanometer or less in size, whilst between 1 nm and 100 nm, therein lies materials that can be considered nanocomposites and beyond the 100 nm mark, there exists macrocomposites and other materials.¹⁴

The consolidation of organic and inorganic materials and in some instances, metals, has often been undertaken to produce new materials that display improved properties, additional utilities or a combination of the two. This form of engineering in which materials are carefully selected for their distinct properties or features resulted in the development of an additional classification system, one that is founded on functionality. Based on this approach, Hagiwara and Suzuki differentiated between composites and hybrids with composites being inferior to hybrids based on their properties and/or usability. Categorization derived from this line of thought gave rise to these categories: structurally-hybridized and functionally-hybridized materials, and materials hybridized through a chemical bond. These categories, constructed by Nanko, have structural hybridization as the centre for the other two in which structural hybridization gives rise to functional hybridization through the merging and enhancement of features whilst hybridization through bond-formation focuses on the actual atoms involved in the formation of these hybrids at an atomic level.¹³

2.1 Synthesizing hybrid materials

A significant amount of research has been carried out in seeking to develop efficient catalysts at a low cost. Various pathways have been identified in the fabrication of hybrid materials to produce multi-functional compounds as it has been established that certain synthetic routes have a significant influence on the properties of these hybrids. Factors such as the size, shape and stability have been noted to affect the functionality of hybrid materials.¹²

Organic-inorganic hybrids, as the term suggests, are composed of both organic and inorganic constituents. Within this category, they are divided into two types based on how the materials interact with one another.¹² Class I hybrids are bound together by intermolecular forces such as hydrogen bonding and π - π interactions whilst class II hybrids have the different entities bound together through covalent or coordination bonds.¹⁵ The production of these hybrids can be achieved in several ways including the sol-gel route, the interpenetration of networks (IPNs),

in situ polymerization, solvothermal/hydrothermal synthesis, as well as self-assembly/assembling of nanomaterials.^{12,15}

Although the fabrication of hybrids dates back to the 20th century, one method that seemingly revolutionized the entire process is the sol-gel method. The sol-gel method was first reported in 1931 in the synthesis of aerogels, however, its use in the fabrication of hybrids was first documented in 1984.^{16,17} Sol-gel synthesis is a bottom-up approach in which small molecules in a homogeneous solution referred to as a “sol” assume the nature of a polymer by fusing into a 3-dimensional, limitless structure known as a gel.^{12,15}

The sol-gel method is characterized by the sequential condensation and hydrolysis reactions of alkoxide precursors in the presence of a solvent.¹⁵ The products obtained from sol-gel synthesis are highly dependent on the operative conditions in which the reactions take place and subsequent treatment as illustrated in Fig. 2.¹⁸ These processes that govern the structure and properties of the materials synthesized include polymer pyrolysis, colloidal dispersion, Pechini gel methods and non-hydrolytic sol-gel reactions.¹⁹ Based on the different synthetic routes, the sol-gel approach can be adopted for the synthesis of a wide range of hybrid materials including metal-organic hybrids,²⁰ biohybrids,^{20,21} silica-polysaccharides,²² and polymer-silica hybrids.²³

The interpenetration of networks is a method that lends itself to sol-gel synthesis in that the hybrid preparation involves polymerization of a monomer in a sol-gel.^{15,24} The second alternative involves an already-existing polymer that is subjected to the conditions of a sol-gel procedure whereas with the third route, functionalized organic precursors are used to initiate the formation of new networks.^{15,25,26}

IPNs are the result of either crosslinking between organic and inorganic polymer networks forming simultaneously, the emergence of a secondary polymer network from the primary one or through the bond-formation between the separate entities.¹⁵ The first two are descriptive of Class I IPNs where the hybrids have weak bonds between them whilst the third is representative of Class II IPNs characterized by the existence of covalent bonds between the organic and inorganic materials.¹⁵

In situ polymerization is another method often used in the synthesis of hybrids. This method involves the polymerization of a mixture composed of either a single or multiple monomers. During the polymerization process, covalent bonds are forged between the organic and inorganic constituents of the mixture.¹² As the method suggests, it is often applied in the fabrication of inorganic-polymer composites derived from polymers and metal oxides.¹⁵ It is worth noting that the inclusion of metals in organic-inorganic polymers only yields hybrids when there are covalent bonds formed. In cases where the metal ions interact with the organic constituents through coordination bonds such as metal-centred polymers and metal-coordinated monomers, the polymers formed are not regarded as hybrids but rather metal-containing polymers.²⁷

The hydrothermal and solvothermal approaches to hybrid synthesis are alike with the only difference being that the former involves an aqueous medium as the solvent whilst the latter is inclusive of both

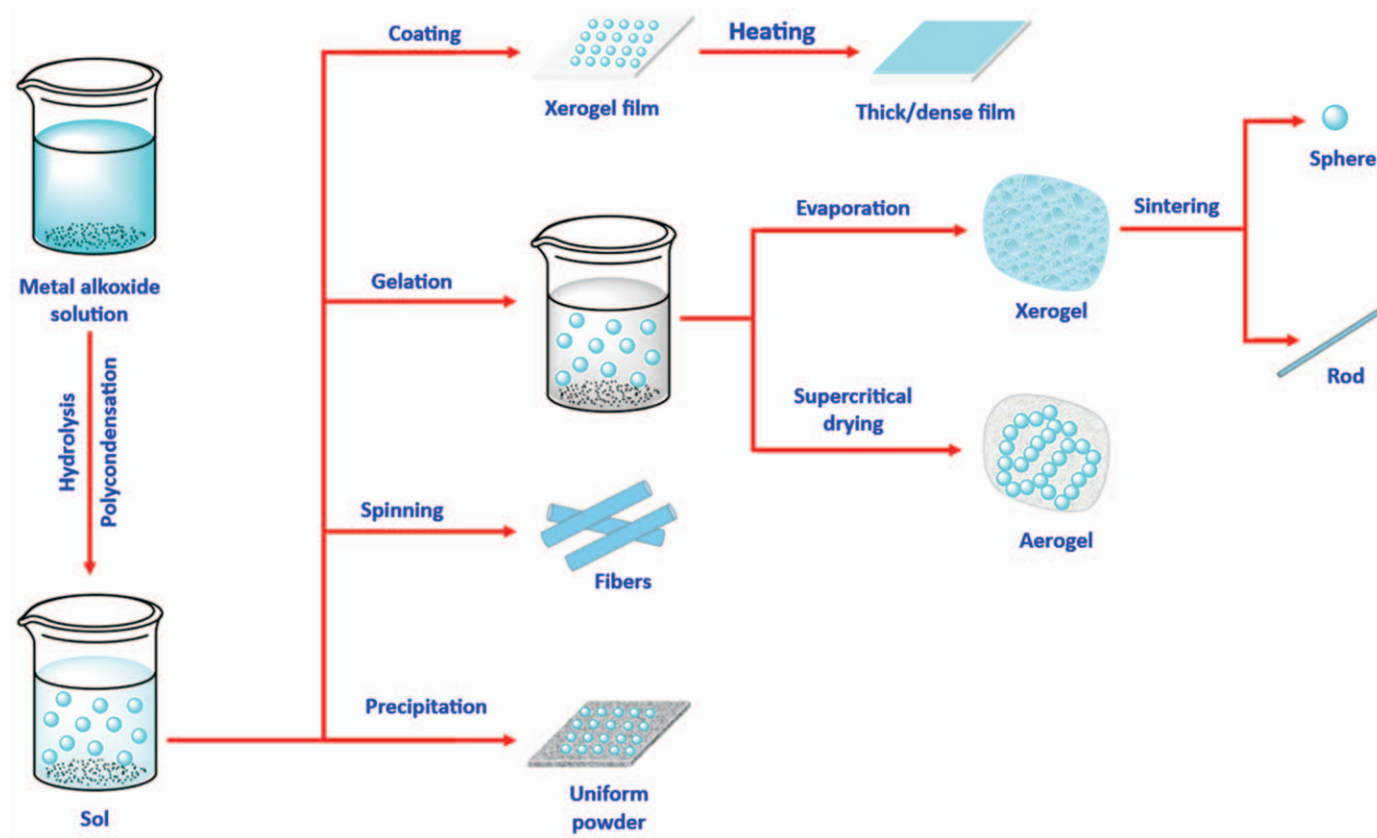


Fig. 2 An illustration of how the reaction conditions in sol–gel synthesis yield various materials.

aqueous and non-aqueous media as solvents.^{12,28} Regardless of the nature of the solvent, whether it is aqueous or non-aqueous, both methods produce hybrids through reactions between the precursors in a sealed vessel at high temperatures and high pressures.¹² Depending on both the temperature and the pressure, the system can be heterogeneous or homogeneous, and furthermore, subcritical or supercritical.²⁸

Self-assembly and the assembling of nanomaterials are similar methods to preparing hybrids which involve starting with small molecules to build larger particles.^{12,15} The distinction between the two is that the self-assembly method is spontaneous and yields highly ordered materials that are without covalent bonds whilst the assembling of nanomaterials is non-spontaneous and entails the sequential deposition of one material over another with a different composition.¹⁵ Despite the versatility offered by these methods in terms of variations in the final composition and thickness of films produced, the methods are plagued by poor reproducibility as well as scalability.¹² It is for these reasons that these methods are often limited to the production of core-shell nanocomposites and/or metal-organic frameworks (MOFs).^{12,15}

On its own, self-assembly is highly sophisticated as it gives rise to synthesis through the construction of hierarchical structures. Hierarchical structures are composed of starting materials that evolve into more complex structures as the levels of construction increase.¹⁵ Biohybrids are common examples of hierarchical structures in which each subsequent addition introduces new properties into the overall structure.²⁹ Table 1 provides a summary of the advantages and

Table 1 Advantages and disadvantages of the methods related to the fabrication of hybrid materials.

Method	Advantage(s)	Disadvantage(s)	Ref.
Sol-gel	• Cost-effective • Ideal for complex structures	• Time-consuming • Products susceptible to shrinkage	12
<i>In situ</i> polymerization	• More control on the morphology • Improved mechanical stability	• Not always reproducible • Difficult to upscale	12 and 15
Solvothermal/hydrothermal	• More control on the morphology • High level of crystallinity	• Specialized reaction equipment required • Limited control over reaction kinetics	12
Self-assembly/assembling of nanomaterials	• Products can be tuned to a specific function	• Not always reproducible • Limited material selection	12 and 15
Interpenetration of networks	• Biocompatible • Low toxicity • Biodegradable	• Difficult to upscale	30

disadvantages associated with each of the synthesis methods described in this chapter.^{12,15,30}

3 Common reactions for energy conversion

For many years, single-atom catalysts derived from metals have been at the forefront of all forms of catalysis.^{31,32} Having demonstrated their high catalytic abilities, metals have served as a foundation in the design and construction of hybrid materials for catalysis.^{33,34} In terms of electrocatalysis and photoelectrocatalysis, hybrid materials have been reported extensively for various reactions including the reduction of CO₂ (CO₂RR), the oxidation of CO (COOR), the reduction of N₂ (NRR) and the electrolysis of water which is inclusive of both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER).³⁴ For the purpose of this chapter, the hybrids used in electrochemical sensing will not be discussed. Due to the various analytes that exist, the number of hybrid catalysts and mechanisms to consider would require a separate review.

3.1 CO₂ reduction reaction

The CO₂ reduction reaction, often abbreviated as CO₂RR, is a mild reaction that is designed to convert carbon dioxide into more viable fuels such as ethanol and ethylene in aqueous conditions.^{35,36} The reaction itself is plagued by slow reaction kinetics that enable carbon-carbon (C-C) bond formation. Based on the reported mechanism, C-C coupling is a thermochemical step that involves neither proton nor electron transfer. As such, the reaction energy does not decrease as a result of polarization on the surface of the catalyst.³⁷ To address this issue, a variety of materials have been studied in an attempt to improve the rate at which CO₂RR proceeds.³⁸ In many cases, adsorption of the *CO intermediate onto the catalyst has been established as being a critical factor in enabling C-C bond formation. The disadvantage however, to lowering the binding energy between the intermediate and the surface of the catalyst, is that *CO desorption is favoured over C-C coupling.³⁷ For CO₂RR, copper as a single atom catalyst has demonstrated the most efficiency however, the trajectory in the design and fabrication of catalysts for CO₂RR has changed and migrated towards organic-inorganic and inorganic-inorganic hybrids.^{39,40} The decision to opt for hybrids for this type of reaction, in addition to improving the reaction kinetics, is the need for stable catalysts that do not lose their structural integrity following continuous use which is something that copper as a single-atom catalyst fails to do.³⁹

Table 2 provides some examples of hybrid materials applied in the electrochemical and photoelectrochemical reduction of CO₂.⁴¹⁻⁵¹ In studying the efficiency of catalysts for the CO₂RR, several parameters are often investigated with the onset potential, overpotential and the faradaic efficiency being significant markers of a good catalyst. The onset potential is the potential applied to the catalyst to enable the detection of carbon monoxide, which is one of the products of the CO₂RR.³⁸ The overpotential is the difference between the onset potential and the equilibrium potential

Table 2 Hybrid materials applied in the electrochemical and photoelectrochemical reduction of CO₂.

Catalyst ^a	EC/PEC	Onset potential	Current (mA cm ⁻²)	FE (%)	Electrolyte	Ref.
In ₂ O ₃ -rGO	EC	−1.2 V vs. SHE	^b	84.6	0.1 M KHCO ₃	41
In ₂ O ₃ /PC	EC	−1.18 V vs. RHE	251.4	95.4	1.0 M KOH	42
CoPcS/GO-COOH	PEC	−1.0 V vs. Ag/AgCl	1.5	83.9	0.1 M KHCO ₃	43
FTO mesoITO CoPcP	PEC	−1.09 V vs. SHE	1.3	91 ± 3	0.5 M KHCO ₃	44
Au/Py-CNTs-O	EC	−0.98 V vs. RHE	3.16 × 10 ^{−5}	93	0.1 M KHCO ₃	45
[Co(qpy)] ²⁺ @MWCNTs	EC	−0.35 V vs. RHE	0.94	100	0.5 M NaHCO ₃	46
Cu@AlO _x NCs	EC	−1.1 V vs. RHE	2.7 ± 0.3	20	0.1 M KHCO ₃	47
N-Fe ₃ C/rGO-20	EC	−0.3 to −0.4 V vs. RHE	20.8	34.2	0.5 M KHCO ₃	48
rGOAu	EC	−0.24 V vs. RHE	0.02	^b	0.5 M NaHCO ₃	49
Bi/Gr	EC	−0.97 V vs. RHE	28.1	92.1	0.5 M KHCO ₃	50
Pt-rGO-TNT	PEC	2 V	^b	78	1 M NaCl and 1 M Na ₂ SO ₄	51

^a PC – In₂O₃/poly(3,4-ethylenedioxythiophene)-modified carbon; FTO|mesoITO|CoPcP – phosphonic acid-bearing Co phthalocyanine on mesoporous TiO₂ on a fluorine-doped SnO support; [Co(qpy)]²⁺@MWCNTs – Co quaterpyridine complex/carbon nanotube; Cu@AlO_x NCs – Cu-encapsulated Al nanocrystals; Bi/Gr – Bi NPs on graphene oxide nanosheets; Pt-rGO-TNT – Pt-modified rGO with Pt-modified TiO₂ nanotubes.

^b Not reported.

at which the carbon monoxide is reduced, which is, theoretically, -0.11 V.⁵² An ideal catalyst is one that presents a high, positive onset potential coupled with a small overpotential.³⁸ In comparing the catalysts in Table 2, both the electrochemical and photoelectrochemical, the lowest potential applied/onset potential is observed for both In_2O_3 -rGO and In_2O_3 /PC catalysts.^{41,42} The one thing that both catalysts have in common is the inclusion of In_2O_3 highlighting the role of indium driving CO_2RR . Although the other catalysts are not indium-based as this review is not focused primarily on indium catalysts, they too exhibit great potential for CO_2RR . The absence of lower onset potentials may be attributed to the composition of the catalyst, the electrolyte, or other experimental conditions such as the temperature and/or pressure.^{41–51,53,54}

Although no direct comparisons can be made as the resulting products from the reduction of CO_2 vary from ethylene to formate, based on the catalysts in Table 2, the bulk of the positive responses can be attributed largely to the presence of surface defects which are the result of the inclusion of carbon-based supports and a high ability to adsorb the reactant onto the catalyst's surface.^{37,38,41–51} In addition to that, the interactions at the interface between the carbon supports and the secondary catalyst material may also account for the results observed in the CO_2RR .^{41,43,45–51} Furthermore, owing to the very complex nature of hybrid catalysts, the mechanisms under which CO_2 is reduced electrochemically and/or photoelectrochemically, remain an understudied aspect of the CO_2RR . The mechanisms depend not only on the final product but also on whether the reaction takes place at room temperature or not as CO_2RR suffers from competing with the hydrogen evolution reaction under ambient conditions.³⁸

Of the few reports that have been able to describe the important step regarding the CO_2RR , one report cited that the covalent bond between a phthalocyanine and the graphene oxide enabled a quicker transfer of electrons between the two materials which explains the improvement in the Faradaic efficiency.⁴³ Zhu *et al.* also attributed their results to the fast transfer of electrons permitted by the charge interaction between the two catalyst materials. Along with an improvement in electron-transferring abilities, the interactions at the surface of the indium metal post-reduction of the In_2O_3 were also proposed to lower the adsorption energy of the $^*\text{OCHO}$ intermediates onto the catalyst, which in turn relates to maintaining an active catalyst surface.⁴² Using experimental and theoretical calculations, Zhang and colleagues were able to confirm that the chemical coupling between the In_2O_3 and reduced graphene oxide (rGO) are responsible for stabilizing the $^*\text{OCHO}$ intermediate. In their work, Zhang *et al.* reported that the $^*\text{OCHO}$ intermediate is observed at a lower Gibbs energy and this is largely due to the electron-rich rGO.⁴¹

Roy *et al.* used spectroelectrochemical methods to decipher the mechanism and they found that the absence of a doubly reduced species corresponded to a rate-determining step, the reduction of the $[\text{CoPcP}]^{2-}\cdot\text{CO}_2$ adduct.⁴⁴ In the study involving the Au/Py-CNTs-O catalyst, it was established, through theoretical calculations, that the activation energy of the rate-limiting step can be reduced by coupling the

gold with the pyridine group. Through coupling of these two components of the catalyst, stabilization of the carboxyl intermediate ($^*\text{COOH}$) was observed. This, however, applies only to nitrogen-containing groups that function as proton-acceptors.⁴⁵

Regarding catalysts for PEC specifically, semiconductors that are not based on metal oxides are considered better-suited as they are likely to have a negative conduction-band potential.^{55,56} In the general sense, for CO_2RR through PEC, the first step involves illumination of the catalyst which results in the production of electrons and holes which are required for the electrochemical processes to take place.⁴³ The important part in this regard is that the catalyst be photoactive and be capable of photo-oxidation. Graphitic carbon nitride and phthalocyanines, as reported by Nakada and Neha are some of the most common examples of semiconductors used in PEC that are not metal oxides.^{40,43}

In designing the ideal catalyst for CO_2RR , the catalyst's ability to be reduced with two electrons is considered an important aspect in controlling the catalyst's selectivity as far as the products are concerned. Optimization of the films and their elemental composition as well as altering the oxidation states at the surface where metal catalysts are involved are some of the ways in which hybrid catalyst materials can be designed for CO_2RR . By optimizing the catalyst structures, more studies, as suggested by Cheng *et al.*, involving electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), can be applied in studying the surface catalytic activity of so as to determine the mechanisms involved in the CO_2RR .⁵¹

3.2 CO oxidation reaction

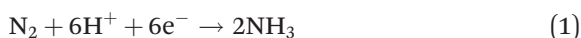
Carbon monoxide oxidation is an important reaction in regulating environmental pollution caused by industrial processes.⁵⁷ The reaction is also crucial in controlling the amount of CO in proton exchange membrane fuel cells (PEMFCs) as the gas has a tendency of poisoning the metal-based catalysts, more so platinum-based.⁵⁸ Similar to catalysts for CO_2RR , catalysts for the CO oxidation reaction (COOR) were based primarily on single atom catalysts however, that has also changed.⁵⁹ Having realized that monometallic catalysts suffer from a decrease in catalytic activity over time, presumably due to the adsorption of intermediates and/or agglomeration, the development of new catalysts for COOR has become more inclusive in its selection of materials with many of the hybrids not being centred around gold despite it demonstrating the best catalytic response, more so under ambient temperatures.^{60–62}

The catalytic oxidation of CO can be performed in various ways including surface polarization as well as through EC and PEC.^{61,63} Although there are a multitude of catalysts that exist for COOR, CO oxidation through electrochemical and photoelectrochemical processes remains an understudied area. At present, the most visible contribution has come from Eid and their colleagues. Using a platinum and palladium co-doped carbon nitride (PtPd/CN) catalyst, Eid *et al.* reported a current density of 14.75 mA cm^{-2} through EC and one of 21.9 mA cm^{-1} through PEC. This

increment was attributed to the small band gap of the carbon nitride (2.7 eV). The overall positive performance of the catalyst was also ascribed to high surface area and conductivity offered by the carbon nitride.⁶³ The lack of hybrid catalysts for COOR through EC and/or PEC may be due to researchers overlooking the process as CO is a strong feature in CO₂RR. It is likely that COOR is accounted for as part of CO₂RR as a whole and not a reaction that requires greater engagement or isolation from all the other steps involved.⁴⁷

3.3 N₂ reduction reaction

The nitrogen reduction reaction (NRR) is a reaction in which nitrogen and hydrogen are used to produce ammonia. The reaction is a single-step reaction that involves a single nitrogen molecule reacting with six protons and six electrons to produce two molecules of ammonia as described in eqn (1).⁶⁴



Due to the inert nature of nitrogen with a dissociation energy of approximately 941 kJ mol⁻¹, using the Haber–Bosch process, the reaction is forced to take place at both a high temperature (400–600 °C) and a high pressure (100–200 atm).^{64,65} And despite the reaction being exothermic, the input energy required to initialize the reaction weighs negatively on this approach hence the continuous search for alternative catalysts.^{64,66} In addition to the high activation energy, the NRR, similar to the CO₂RR, is also plagued by the fact that it competes with the hydrogen evolution reaction, the intermediates that form and the multiple protons required for the reaction to proceed. These hindrances are the main contributors to the slow reaction rates and low Faradaic efficiencies observed for the NRR. In countering these issues, various approaches have been undertaken including the construction of the reactor, the nature of the electrolyte as well as the catalyst itself.⁶⁶ This chapter focuses on the catalyst aspect as everything else depends largely on its abilities.

Ceballos *et al.* highlighted, in their review of catalyst design strategies for NRR, that bimetallic catalysts are an understudied area for NRR, and that transition metal nitrides along with carbon-based supports are a possible solution to improving the reaction's selectivity towards NRR.⁶⁶ In realising this, the construction of catalysts for NRR has migrated from simple, single-atom and bimetallic catalysts to more complex structures that are composed of both organic and inorganic entities.^{66–70} Furthermore, in developing these new materials, the reduction process has also expanded to include photocatalysis where the reduction of ammonia can also be observed through photoelectrochemical means.^{71,72} The catalysts in Table 3 are some of the recent examples of hybrid catalysts for NRR for both electrochemical and photoelectrochemical catalysis.^{67–79} In the earlier years, many NRR hybrids were composed largely of iron coupled with carbon and nitrogen-containing compounds. The more recent hybrids are inclusive of a wider range of elements such as molybdenum, bismuth, ruthenium and non-metallic catalysts such as carbon organic frameworks (COFs) and carbon nanotubes (CNTs).^{68–73}

Table 3 Hybrid materials applied in the electrochemical and photoelectrochemical reduction of N₂.

Catalyst ^a	EC/PEC	Onset potential	NH ₃ yield/rate	FE (%)	Electrolyte	Ref.
NbTiO ₄ @NCNR	EC	−1.2 V vs. SHE	58.13 ± 8 μg h ^{−1} cm ^{−2}	10.4 ± 1.4	0.01 HCl	67
Fe–N/C–CNT	EC	−0.2 V vs. RHE	34.83 μg h ^{−1} mg _{cat} ^{−1}	9.28% at	0.1 M KOH	68
Fe _{SAC} –N–C	EC	−0.1 V vs. RHE	3.47 μg h ^{−1} cm ^{−2}	23.7	0.1 M KOH	69
SA–Ru@NAC	EC	−0.6 V vs. RHE	67.8 ± 4.9 μg h ^{−1} mg _{cat} ^{−1}	19.5 ± 0.6	0.1 M K ₂ SO ₄	70
TiB ₂ @AuNPs	PEC	−0.2 V vs. RHE	535.2 ^b and 491.3 ^c μg mg _{cat} ^{−1} h ^{−1}	32	0.1 M Na ₂ SO ₄	71
BiVO ₄ /PANI	PEC	−0.1 V vs. RHE	0.93 μg h ^{−1} cm ^{−2}	26.43	0.1 M Li ₂ SO ₄	72
COF–Fe/MXene	EC	−0.5 V vs. RHE	41.8 μg h ^{−1} mg _{cat} ^{−1}	43.1	0.1 M Na ₂ SO ₄	73
Co ₉ S ₈ @WS ₂ –900	EC	−0.4 V vs. RHE	50.25 μg h ^{−1} mg _{cat} ^{−1}	46.81	0.1 M KOH	74
MoS ₂ @LZO	PEC	−0.4 V vs. RHE	10.4 μg h ^{−1} cm ^{−2}	2.25	0.1 M KOH	75
CQDs/STO	PEC	−0.30 V vs. RHE	22.37 μg h ^{−1} cm ^{−2}	10.2	0.1 M Na ₂ SO ₄	76
Mo/CTF–I	EC	−0.405 V vs. RHE	7.23 μg h ^{−1} mg _{cat} ^{−1}	27.3	0.1 M KOH	77
BQD/MS	PEC	−0.4 V vs. RHE	18.5 μg mg ^{−1} h ^{−1}	33.2	0.1 M Na ₂ SO ₄	78
MoFe–NC	EC	−0.3 V vs. RHE	28.5 μg mg _{cat} ^{−1} h ^{−1}	39.9	0.1 M Li ₂ SO ₄	79

^a NbTiO₄@NCNR – NbTiO₄ supported on nitrogen-doped carbon nanorods; Fe–N/C–CNT – Fe on carbon and nitrogen carbon nanotubes; Fe_{SAC}–N–C – Fe single-atom on nitrogen-doped carbon nanosheets; SA–Ru@NAC – Ru-loaded 2-amino-1,3-carboxy-azulene metal–organic framework (MOF)-derived N-doped porous carbon; TiB₂@AuNPs – TiB₂ with gold NPs; BiVO₄/PANI – BiVO₄ with polyaniline; COF–Fe/MXene – 1H,1H,2H,2H-perfluorodecanethiol modified carbon organic framework with Fe and an MXene; Co₉S₈@WS₂–900 – Co₉S₈ nanosheets with WS₂; MoS₂@LZO – MoS₂ on La₂Zr₂O₇; CQDs/STO – carbon quantum dots with SrTiO₃; Mo/CTF–I – Mo oxide particles on charge-modulated conjugated triazine framework; BQD/MS – Bi₂S₃ quantum dots with MoS₂ nanoflowers; MoFe–NC – Mo/Fe–nitrogen–carbon.

^b PEC.

^c Simulated sunlight.

In the context of N_2 reduction, the catalyst activity is often assessed through determining the Faradaic efficiency along with the rate at which ammonia is produced or how much ammonia is produced. In both instances, a higher value is preferable. Looking at the FE alone, $Co_9S_8@WS_2-900$ presents the highest efficiency with a value of 46.81% followed by the COF-Fe/MXene hybrid with a value of 43.1%, respectively.^{73,74} Regarding the yield, the highest values in Table 3 are reported for $TiB_2@AuNPs$ with values of $535.2 \mu g mg_{cat}^{-1} h^{-1}$ through PEC and $491.3 \mu g mg_{cat}^{-1} h^{-1}$ under solar simulation, respectively.⁷¹ Further analyses on the rate of NRR cannot be made as the catalysts in Table 3 are based on reports in which either the rate or yield is reported, seldom both. As such, the FE in this case is the only parameter that can be used to make comparisons.^{67–79} From the catalysts presented in Table 3, there are no definitive trends that can be identified as there is no dominant material or element that takes preference over another. Unlike the catalysts associated with CO_2RR , the catalytic activity of NRR catalysts is not entirely dependent on the existence of surface defects but varies with each hybrid. While some reports cite a uniformity in atom dispersion as being a significant contributor to the catalyst activity, others attribute a lack of uniformity in the catalyst surface as being the driving force behind the improved NRR results.^{67–79}

In accounting for the NRR catalyst activity by assessing the structure, both Agour and He, along with their colleagues, ascribed the catalyst activity to the even distribution of iron atoms on the supporting material.^{69,73} He *et al.* further argued that the catalyst's hydrophobic nature along with the presence of nitrogen were significant contributors to the catalyst's ability to produce an FE value of 43.1%. An important note regarding this particular catalyst is that the ammonia produced was entirely from the N_2 gas introduced into the system, and not from the nitrogen-containing support.⁷³ Similar to the work carried out by Agour and colleagues, Wang *et al.* reported the same thing regarding their Fe-N/C-CNT catalyst, that the iron-nitrogen ($Fe-N_3$) centres were the active sites responsible for driving the NRR forward.^{68,69}

For the $MoS_2@LZO$ and $SA-Ru@NAC$ catalysts, surface defects were considered the main reason for the impressive catalytic results observed.^{70,75} The theoretical calculations illustrated, using an optimized structure of the $SA-Ru@NAC$ material, that the catalyst could lower the bond energy of the N_2 molecule through stretching thus initiating the NRR.⁷⁰ The other catalysts on the other hand, were proposed to possess either sulphur or oxygen vacancies on their surfaces which enhanced N_2 adsorption by creating an electron-deficient environment.^{74–79} For the $Co_9S_8@WS_2-900$ catalyst, the density functional theory (DFT) calculations suggest that activation of the N_2 molecule is carried out by the lone tungsten atom along the edge of the sulphur vacancies within the entire catalyst.⁷⁴ This theory was also reported by Hu *et al.* for their PEC catalyst, the CQDs/STO hybrid. In their findings, Hu *et al.* also suggested that due to the oxygen vacancies that exist on the STO, the possibility of the electrochemical reduction of nitrogen taking place concurrently with the photoelectrochemical reduction is high.⁷⁶

Yu and Lin, and their respective colleagues cited the surface interactions between the different constituents of the catalysts as the main contributors in steering the NRR forward. In both reports, molybdenum featured as the metal component where in one case it was supported by a conjugated triazine framework (CTF) whilst in the other, the MoS₂ nanoflakes were coupled with La₂Zr₂O₇ nanofibers to produce a MoS₂@LZO hybrid.^{75,77}

The positive output in the Mo/CTF-I material was ascribed to electron transfer from the Mo to the CTF support. This process was reported to result in the formation of MoOx with a valence state of 5⁺ and further lowered the energy required to transfer the received electrons to the N₂ molecule.⁷⁷ The MoS₂@LZO hybrid, reported for the PEC reduction of nitrogen, is composed of a mixed phase of La₂Zr₂O₇ nanofibers which create an interface that is favoured by oxygen vacancies.⁷⁵ And while the PEC NRR catalyst activity in this regard is attributed to the oxygen vacancies, the notion that this material is not similar to the BiVO₄/PANI hetero-junction in which an alternate band gap exists cannot be disregarded. According to Bai, in the NRR through PEC, the alternating band gap promotes the fast transfer of electrons which presents itself as good catalytic activity with a high selectivity towards the production of ammonia.⁷²

3.4 Water electrolysis

Water splitting, often referred to as water electrolysis, is an electrochemical reaction in which water is split to produce both hydrogen and oxygen. The simplified version of the process is a single-step reaction described by two half-reactions where hydrogen is formed through reduction of protons at the cathode (hydrogen evolution reaction, HER) whilst the oxidation reaction at the anode yields oxygen (oxygen evolution reaction, OER).⁸⁰ Relative to the HER, the OER proceeds at a much slower rate.⁸¹ In overcoming the thermodynamic barrier, various catalysts have been studied with transition metal oxides and perovskites being at the forefront as far as alternatives to platinum-group metals are concerned.^{81,82}

The hydrogen evolution reaction is composed of two electrochemical steps, the dissociation of water to produce a hydroxide and an adsorbed proton as the first step and the formation of hydrogen as the second step. The first step is often referred to as the Volmer step (eqn (2)) whilst the second in which hydrogen is produced, can proceed either according to the Tafel equation (eqn (3)) or according to the Heyrovsky equation (eqn (4)).⁸¹



Theoretically, in alkaline media, as described by eqn (2)–(4), the rate-determining step for the hydrogen evolution reaction is the Volmer step however experimentally, it is not always the case due to the nature of the catalyst (and the reaction conditions, either acidic or basic).⁸³ Although

single-atom catalysts have displayed the greatest efficiency regarding this reaction, the majority have been based on noble metals such as platinum, iridium and palladium. These metals, being expensive and scarce in their nature, has prompted the need for less expensive, more earth-abundant alternatives.⁸² In developing these alternatives, hybrids with suitable OH* adsorption sites have been identified, amongst other factors, as being important as an abundance of this character from a material can stimulate the rate at which the hydrogen evolution reaction proceeds.^{84–87} In this review, the Ni⁰–Ni(OH)₂ catalyst is one that explicitly adheres to this criterion. In their description of how the catalyst functions, it is reported that the dissociation of water is accelerated by the Ni^{III}'s intense adsorption of OH* with a reduced affinity for the H* species by the Ni⁰.⁸⁸

An ideal catalyst for water splitting is one that presents a low overpotential, a small Tafel slope value and in general, a high current density.⁸⁹ The Tafel slope, derived from the Tafel equation, relates the electrochemical reaction to the overpotential and is critical in deciphering the reaction mechanisms under which reactions proceed.^{89,90} In the case where a Tafel slope value of 120 mV per decade is recorded, based on the three primary steps under which HER proceeds, the rate-determining step would be the Volmer step in which there is proton adsorption. For catalysts that exhibit Tafel slope values of 60 mV per decade or less, the rate-determining step would either be the Tafel or Heyrovsky step.⁹⁰ From the materials provided in Table 4, for both the electrochemical and photoelectrochemical hydrogen evolution reaction, the overpotentials range from –0.1 V to 0.26 V whilst the Tafel slope

Table 4 Hybrid materials applied for HER through electrochemical and photoelectrochemical methods.

Catalyst ^a	EC/PEC	Overpotential	Tafel slope (mV dec ^{–1})	Electrolyte	Ref.
Ni ⁰ –Ni(OH) ₂	EC	39 mV vs. Hg/HgO	32	1 M KOH	88
Fe/P/C NWs	EC	256 mV vs. RHE	^b	0.5 M H ₂ SO ₄	91
CoS ₂ @WS ₂	EC	–97.2 mV vs. RHE	66.0	0.5 M H ₂ SO ₄	92
CoS ₂ /CoSe ₂ /DETA	EC	80 mV vs. RHE	33.6	0.5 M H ₂ SO ₄	93
WS ₂ /graphene/ NFs	EC	~0.1 V vs. RHE	43	0.5 M H ₂ SO ₄	94
FeS ₂ -rGO	EC	226 mV vs. RHE	61	0.5 M H ₂ SO ₄	95
CoSe ₂ -CNTs	PEC	163 mV vs. RHE	69.4	0.5 M H ₂ SO ₄	96
MoS _x /NCNTs	EC	75 mV vs. RHE	40	0.5 M H ₂ SO ₄	97
MoS ₂ /Si and MoSe ₂ /Si	PEC	^b	^b	0.1 M H ₂ SO ₄	98
GaN NW/Si	PEC	^b	^b	0.5 M H ₂ SO ₄	99

^a Fe/P/C NWs – Fe, carbon and phosphorous nanowires; CoS₂@WS₂ – CoS₂ nanosheets with WS₂; CoS₂/CoSe₂/DETA – CoS₂/diethylenetriamine nanobelts with CoSe₂ NPs; WS₂/graphene/NFs – WS₂ NPs on graphene nanofibres; FeS₂-rGO – iron sulphide NPs on reduced graphene oxide; CoSe₂-CNTs – CoSe₂ NPs on a carbon nanotube support; MoS_x/NCNTs – MoS_x NPs on a nitrogen-doped carbon nanotube support; MoS₂/Si and MoSe₂/Si – MoS₂/Si and MoSe₂/Si NPs on Si NPs; GaN NW/Si – GaN nanowires on Si support.

^b Not reported.

values lie between 32 mV per decade and 69.4 mV per decade, suggesting that all these hybrids subscribe to the Tafel–Heyrovsky step as the rate-determining step.^{88,91–99}

Due to the mechanism of HER being simplified by the Tafel slope through inferences, there are limited accounts that provide more detailed mechanisms regarding how the catalysts function and how each entity within the hybrid contributes. Apart from a high level of electrical conductivity, much of the catalytic activity in this regard is attributed to the materials having a form of synergy between them.^{88,91–99} Li *et al.* are a few who have sought to provide an alternative explanation other than synergy between the materials. Using X-ray photoelectron spectroscopy (XPS) and theoretical methods, they suggested that the high catalytic performance is due to the F–P, Fe₃C@C units, and P–C bonds that serve as active sites on the catalyst. In their assessment, they also noted that the Fe–O–P bond is inactive in the electrocatalysis process.⁹¹

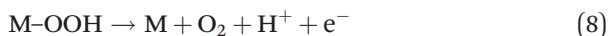
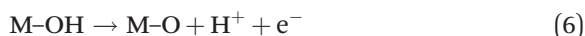
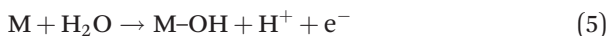
Cobalt and tungsten are some of the more promising candidates for HER not involving noble metals. The catalysts CoS₂@WS₂, CoS₂/CoSe₂/DETA and WS₂/graphene/NF have been reported as excellent HER catalysts with the formation of interfaces at the nanoscale being suggested as the main reason for the high catalytic activity for the CoS₂@WS₂ catalyst, a feature that does not exist when the CoS₂ and WS₂ are studied independently.^{92–94} The CoS₂/CoSe₂/DETA catalyst is composed of a CoSe₂/DETA component upon which the CoS₂ nanoparticles are dispersed. This controlled distribution of CoS₂ onto the CoSe₂/DETA structure allows for regulation of the CoS₂ active sites which fuels the hydrogen evolution reaction.⁹³ Regarding the WS₂/graphene/NF material, the activity of the WS₂ is enhanced by the graphene sheet which may also be applicable to the FeS₂-rGO as both hybrids feature graphene which is known to be a highly conductive material.^{94,95}

Carbon nanotubes (CNTs) are an alternative to graphene as the materials possess similar chemical properties. The most evident difference between the two lies in their shape, the other is in the form of a flat sheet of a highly conjugated system of π electrons whilst the other is in the form of a tube.¹⁰⁰ Pi *et al.* reported on the use of a CoSe₂-CNT PEC catalyst in which CoSe₂ was coupled with pristine CNTs. In their findings, Pi *et al.* attributed the positive catalyst activity to the highly conductive nature of the CNTs, a high level of active sites on the CoSe₂ component, synergy between the two materials that make up the hybrid and the light energy that enhances electron-involvement in the reaction.⁹⁶

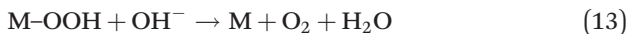
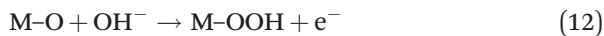
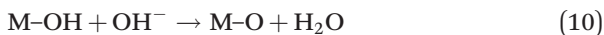
A similar report was produced by Li in which nitrogen-doped CNTs (NCNTs) were coupled with MoS_x as an electrocatalyst for HER. The improvement observed in the hybrid was simply attributed to the materials complimenting each other with the NCNTs being of great significance in the transportation of electrons.⁹⁷ In an alternate PEC case involving molybdenum in MoS₂/Si and MoSe₂/Si, the light energy was considered the driving force in the improved catalytic activity whilst in the case of the GaN NW/Si catalyst, both the light and the catalyst morphology contributed to the enhanced catalytic activity.^{98,99} Based on their theoretical calculations, the surface of the GaN is transformed into a Ga–O–N species

that possesses metallic properties which increased the number of active sites on the catalyst surface, which not only improved the catalytic activity but further induced a prolonged stability of the catalyst.⁹⁹

The oxygen evolution reaction makes up the second half of the electrolysis of water and as mentioned before, it is kinetically unfavoured as it proceeds at a slow rate. The primary reason for this is because a minimum of four electrons needs to be transferred in order to produce the oxygen–oxygen double bond.⁸¹ Many of the active sites for OER are located on the catalyst with intermediates such as OH*, O*, and OOH* also attaching to those same sites as the reaction progresses (asterisk and M used interchangeably to refer to the electrode/catalyst). The OER mechanism can be explained in two different ways depending on the reaction conditions, whether they are acidic or alkaline.¹⁰¹ Under acidic conditions, the first step entails adsorption of the water molecule onto the catalyst to produce an adsorbed OH* species. This is accompanied by the removal of an electron in conjunction with a H⁺. The M–OH undergoes an oxidation step to produce an adsorbed oxygen O* (M–O), a second H⁺ and a second e[−]. The second-last step entails the O* species reacting with a secondary water molecule to yield M–OOH which is then oxidized in a single-electron transfer process to produce oxygen. The procession of events can be described according to the following equations (eqn (5)–(8)).¹⁰²



In alkaline media, the OH[−] is adsorbed onto the catalyst (M in this case) and then oxidized into OH* (eqn (9)). The newly formed OH* species reacts with another OH[−] to produce H₂O and an adsorbed O* which then reacts with another OH[−] to form OOH* (eqn (10)–(12)). The resultant OOH* reacts further with OH[−] to produce O₂ and H₂O as the final products as expressed by eqn (13).¹⁰¹



In utilizing solar energy simultaneously with electrochemical processes, the first step in the mechanism entails light absorption at the anode followed by excitation of the electrons from the valence band to the conduction band which are then separated to the various active sites on the catalyst. Through the application of an external voltage, the OER is

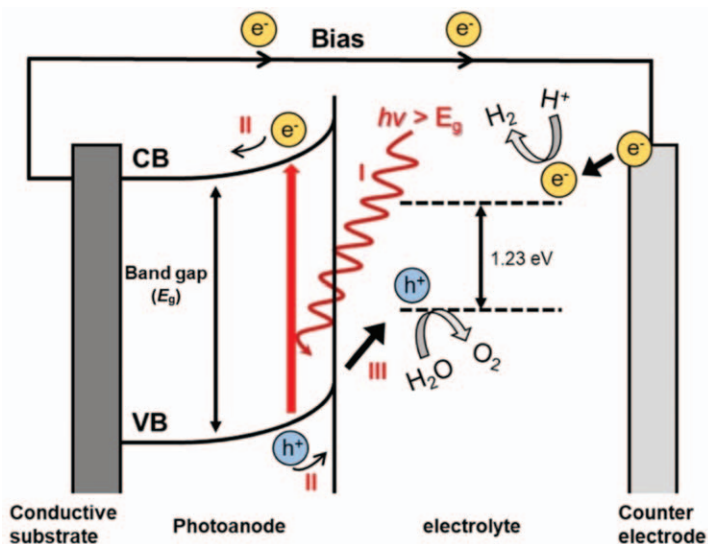


Fig. 3 Schematic illustration of water electrolysis through PEC where step I entails the absorption of light, step II being the separation of the photocarriers and subsequent transportation followed by step III where OER is initiated. Reproduced from ref. 81 with permission from Elsevier, Copyright 2024.

initiated when holes are generated at the surface of the catalyst as a result of the electrons being released into the reaction cycle (Fig. 3).⁸¹ In order for PEC to function effectively, it is important to ensure that there is minimal to no charge recombination once the charge carriers have been liberated from the valence band. To address these issues, various hybrid materials have been synthesized and evaluated as catalysts for OER.^{81,103}

Similar to HER, apart from minimizing or eliminating charge recombination, another factor that has sought improvement is that of the overpotential in which a lower value is more desirable than a higher one. Whilst there are a multitude of hybrids that exist for OER, Table 5 focuses on a select few with the subsequent discussion being centred on the catalyst material(s) and how they have contributed to improving the current density. Synergy is often involved in how hybrid materials behave however it is not always the only factor to consider.^{82,91,104–116}

MXenes are some of the few materials that have been identified as leading candidates in OER due to their large surface area and high surface tunability.⁸¹ As such, they are a recurring feature in Table 5 as seen with the $\text{Co}_3\text{O}_4/\text{Ti}_3\text{C}_2$ MXene, $\text{MoO}_x/\text{MQD}/\text{BiVO}_4$ and $\text{BiVO}_4@\text{FhMXene}$ catalysts.^{103–105} In each case, the positive PEC activity is attributed to the highly conductive nature of the MXenes as well as their ability to inhibit charge recombination. In the case of $\text{Co}_3\text{O}_4/\text{Ti}_3\text{C}_2$ MXene, the inclusion of Co_3O_4 plays a significant role in restricting charge recombination by covering the defective sites on the catalyst.¹⁰⁴ Regarding the $\text{BiVO}_4@\text{FhMXene}$ material, the combination of the ferrihydrite (Fh) with MXene on a BiVO_4 platform was suggested as the driving force in the improved catalytic behaviour with the MXene being able to alter the work

Table 5 Hybrid materials applied for OER through electrochemical and photoelectrochemical methods.

Catalyst ^a	EC/PEC	Current (mA cm ⁻²)	Electrolyte	Ref.
CeO ₂ /Co(OH) ₂	EC	17.6	1.0 M KOH	82
Fe/P/C NWs	EC	1.56	1 M KOH	91
Co ₃ O ₄ /Ti ₃ C ₂ MXene	PEC	5.05	1.0 M borate buffer	104
MoO _x /MXene	PEC	5.85	0.5 M KBi	105
BiVO ₄ @FhMXene	PEC	4.55	0.5 M Na ₂ SO ₄	106
P-Fe ₂ O ₃	PEC	2.5	0.1 M KOH	107
TiO ₂ /rGO/NiFe-LDH NAs	PEC	1.74	0.5 M Na ₂ SO ₄	108
MnCo ₂ O ₄ @NiFeRu-LDH	EC	100	1 M KOH	109
FeNi/SN-C	EC	3.4	1 M KOH	110
TiO ₂ /P-C ₃ N ₄ /Co ₃ O ₄	PEC	1.18	0.5 M Na ₂ SO ₄	111
Mn ₂ O ₃ /PVA/rGO and Mn ₂ O ₃ /TOPO/rGO	EC	7–11	0.1 M KOH	112
C-Pd-MTOx-3DG	EC	19.8	1.0 M KOH	113
(P)-Thiadiazole-[7]helicene embedded NiO _x	EC	^b	0.1 M KOH	114
NF-VCs	EC	100	1.0 M KOH	115
DN gel	EC	1	0.5 M H ₂ SO ₄	116

^a Fe/P/C NWs – Fe, carbon and phosphorous nanowires; Co₃O₄/Ti₃C₂ MXene – Co₃O₄ MXene; MoO_x/MXene – molybdenum oxide MXene; BiVO₄@FhMXene – ferrihydrite-containing MXene on bismuth vanadate support; P-Fe₂O₃ – phosphorous-doped hematite; TiO₂/rGO/NiFe-LDH NAs – reduced graphite oxide and NiFe layered double hydroxide (LDH) on TiO₂ nanorod arrays; MnCo₂O₄@NiFeRu-LDH – MnCo₂O₄ nanoneedles and NiFeRu layered double hydroxide nanosheets on nickel foam; FeNi/SN-C – FeNi alloy on sulphur and nitrogen-doped carbon support; TiO₂/P-C₃N₄/Co₃O₄ – TiO₂ nanorod arrays capped with phosphorous-doped graphitic carbon nitride and Co₃O₄ nanodots; Mn₂O₃/PVA/rGO and Mn₂O₃/TOPO/rGO – Mn₂O₃ on rGO support derived from *n*-trioctylphosphine oxide and polyvinyl alcohol as controlling agents; C-Pd-MTOx-3DG – carbon-palladium quantum dot-supported manganese-titanium oxide; NF-VCs – nickel foam etched with violet crystal; DN gel – dual network gel.

^b Not reported.

function of the ferrihydrite constituent and enhancing water adsorption. In their observations, Bai *et al.* reported the BiVO₄@FhMXene anode as having a better response than BiVO₄ alone.¹⁰⁶

Iron is another recurring fixture in the table with it being part of the five from the fifteen hybrids provided in Table 5.^{91,106–110} In the Fe/P/C catalyst for OER through electrocatalysis, the F–P bond is cited as the main reason for enhanced catalytic behaviour.⁹¹ In comparing this catalyst to the P-Fe₂O₃ catalyst, considering that both catalysts have a similar composition, it can be argued that in both cases, as suggested for P-Fe₂O₃, that the addition of phosphorous resulted in a shift of the band structure towards more positive potentials which improved the OER activity.^{91,107} And this improvement was further heightened in PEC for P-Fe₂O₃ due to the inclusion of light as it quickened the rate at which the charge carriers and electron holes are transported.¹⁰⁷ It is worth noting that while the OER activity in Fe/P/C was ascribed largely to the Fe–P bond, this bond was not observed in P-Fe₂O₃ upon investigation with XPS.^{91,107} As such, Wang *et al.* suggested that the absence of this bond enhanced the *n*-character of the material through the direct

reduction of Fe_2O_3 by the phosphorous as it reacts with the oxygen on the surface of the iron oxide.¹⁰⁷

In the case of $\text{TiO}_2/\text{rGO}/\text{NiFe-LDH}$ NAs, iron is not the element that carries the most influence, but it is, according to Ning and colleagues, the synergy between rGO and NiFe-LDH in which the oxidation of water is boosted.¹⁰⁸ The same applies to a similar catalyst, $\text{MnCo}_2\text{O}_4@\text{NiFeRu-LDH}/\text{NF}$, where instead of iron, the MnCo_2O_4 and NiFeRu-LDH function in a complementary manner.¹⁰⁹ The conductive nature of iron is most notable in FeNi/SN-C where it is posited that the improved catalytic output is the result of the catalyst structure in which iron is encapsulated in an FeNi shell that is functionalized with sulphur and nitrogen-doped carbon. According to Liu and co-workers, this particular configuration of elements results in stabilization and further activation of the active sites that become apparent as the reaction progresses. Furthermore, the OER activity is heightened due to the doped carbon matrix's extensive surface area as well as the FeNi alloy.¹¹⁰

In a separate case involving a $\text{Co}_3\text{O}_4/\text{P-C}_3\text{N}_4/\text{TiO}_2$ photoanode, the improved OER activity was attributed to a reduction in the diffusion length of the conductive surface and photogenerated holes along with the small size of the Co_3O_4 nanodots. In their argument, Zhongrui *et al.* suggested that this reduction enhanced electron transfer and lowered the likelihood of recombination. In describing the mechanism, the Co_3O_4 nanodots are the most active as the catalytic active sites are located on them. According to the report, the redox reaction of the Co(III/IV) species by the photogenerated holes results in the formation of Co(IV)-O which is reduced to Co(III) . While this happens, there is also the release of oxygen molecules when the Co(IV)-O binds with other OH^- ions.¹¹¹

The 3D framework in conjunction with the reduced graphene oxide was considered the main factor in how $\text{Mn}_2\text{O}_3/\text{PVA}/\text{rGO}$ and $\text{Mn}_2\text{O}_3/\text{TOPO}/\text{rGO}$ behaved as OER catalysts.¹¹² Manganese on its own does not present a great deal of catalytic influence in OER and this is extended to the MTOx-3DG catalyst as well which is capable of both OER and the oxidation of ethylene glycol. In the carbon-palladium quantum dot (C-Pd)-supported manganese-titanium oxide/3D graphene composite, the high catalytic activity is reported to be the result of the reduced particle size of the carbon-coated palladium nanoparticles. Doping with carbon improves the interaction between the palladium and the MTO/3DG support.¹¹³

In other separate reports, the increment in oxygen vacancies in $\text{CeO}_2/\text{Co(OH)}_2$ was reported as the primary contributor to the positive OER activity whilst for the (*P*)-thiadiazole-[7]helicene- NiO_x , the presence of chiral centres fuelled the catalyst activity.^{82,114} Regarding the (*P*)-thiadiazole-[7]helicene- NiO_x catalyst, the group further postulated that the length and functional groups that make up the molecule are important in how the catalyst interacts with the substrate which is worth noting for the design of new catalysts, especially those that are not metal-based.¹¹⁴ Thangasamy's group adopted an alternative approach to designing the organic-inorganic catalyst where crystal violet was deposited

into nickel foam through etching to produce a crystal-violet nickel foam (CV-NF) hybrid. The impressive OER activity was said to be due to the increased catalyst activity sites that are created through the inclusion of the crystal violet dye.¹¹⁵

A non-metallic OER catalyst is presented in Table 5 as a polymeric dual network gel (DN gel) composed of polypyrrole and cyano-bearing groups. The XPS, X-ray absorption fine structure (XAFS) spectroscopy and theoretical calculations suggest that both the organic and inorganic interconnected polymers complement each other in that they are more intertwined than they are coordinated and so there are more vacant bonds that are able to interact with the water. Furthermore, the structural arrangement improves electron transfer through increasing the surface area.¹¹⁶

4 Summary and outlook

The need for sustainable energy sources has prompted a surge in the design and development of new catalysts to facilitate the transition from fossil fuels to cleaner alternatives such as hydrogen from water splitting. And while the electrolysis of water appears to be at the forefront in this regard, it is important to consider other potential sources of fuel not limited to water splitting. In doing so, it has been established that hybrid nanomaterials are quite flexible in various energy-conversion reactions however, there is no hybrid catalyst that can be considered a standard for the rest to be compared with. From this observation, it can be inferred that the synthetic routes for hybrid materials need to be optimized further to enable upscaling. Furthermore, perhaps there is also a need for selection rules regarding the materials for constructing hybrid catalysts to streamline the process. It is evident that MXenes and electron-rich carbon and nitrogen-based catalysts make for good supports in the processes discussed in this review however, it is not always guaranteed that the support will complement the secondary, tertiary and in some instances, the quaternary element of the overall catalyst. As far as future research is concerned in the construction and application of hybrid materials as catalysts for EC and PEC reactions, the following factors should be considered:

- Size is important as illustrated with nanomaterials eliciting different properties from their bulk counterparts. However, it is also important that the catalyst is not too small. The size of the catalyst as a single particle as this may affect how much of the substrates and/or intermediates adsorb onto the surface.
- Although it is unwise to adopt a “one-size-fits-all” approach to catalysis, in the case of hybrid catalysts, it may be of help in understanding why a catalyst would behave in the way it does if it were exposed to different reactions such as NRR, OER and HER. This may provide an alternate way to identifying the active sites and inactive sites, and if some active sites only become apparent as a result of a specific reaction.

- Elemental composition is another factor that may require further investigation in the future as it has been demonstrated that the catalytic activity is affected by how much of a certain element there is in the whole.^{74,91}
- Inclusion of more theoretical calculations to better understand the synergy that exists between the various components of the catalyst across the various reactions, CO₂RR, COOR, NRR, HER and OER.

In general, this review has provided a brief overview of the various hybrid catalysts used for CO₂RR, NRR, HER and OER and has sought to summarize the catalytic activity behind the functioning of these materials without reducing it to synergy. The review has also highlighted how both electrocatalysis and photoelectrocatalysis have evolved from relying on single-atom catalysts based on noble metals to being able to elicit better responses from hybrids fashioned from earth-abundant materials. Overall, an understanding of how each component contributes to the overall functioning of a catalyst is crucial to overcoming the current challenges associated with catalysts for CO₂RR, NRR, HER and OER.

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