Heterostructures Based on 2D Materials: A Versatile Platform for Efficient Catalysis

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The unique structural and electronic properties of 2D materials, including the metal and metal-free ones, have prompted intense exploration in the search for new catalysts. The construction of different heterostructures based on 2D materials offers great opportunities for boosting the catalytic activity in electro(photo) chemical reactions. Particularly, the merits resulting from the synergism of the constituent components and the fascinating properties at the interface are tremendously interesting. This scenario has now become the state-of-the-art point in the development of active catalysts for assisting energy conversion reactions including water splitting and CO₂ reduction. Here, starting from the theoretical background of the fundamental concepts, the progressive developments in the design and applications of heterostructures based on 2D materials are traced. Furthermore, a personal perspective on the exploration of 2D heterostructures for further potential application in catalysis is offered.

1. Introduction

Apart from size effect, dimensionality is also considered as an indispensable parameter in exploring the properties of materials.¹ For instance, allotropes of carbon such as graphite, graphene, carbon nanotube, and fullerene appear as 3D, 2D, 1D, and 0D, respectively, and demonstrate distinct physical and chemical properties. The discovery of graphene in 2004 by Geim and co-workers² has offered an opportunity to investigate various points in scientific research and engineering fields based on other 2D materials.³ Particularly to the context of catalysis, the design of 2D catalysts paves a promising way for excellent performance in activity, stability, and selectivity toward catalyzing a given reaction. Experimental and theoretical researches conducted so far reveal the fact that ultrathin 2D materials possess fascinating advantages in catalysis.⁴⁻⁷ First and for most, 2D geometry renders the materials considerably exposed surface area, which is more pronounced by reducing the thickness, eventually easing the contact between catalyst surface and the adsorbate. Moreover, the interior atoms could be brought to surface when the thickness is decreased to monolayer. Thus, more active sites would be availed for catalysis. To be noted, there is also a great possibility of introducing defects, unsaturated sites, and/or active edges during the formation of ultrathin structures. Under these conditions, the adsorption–desorption energy barrier is sequentially regulated and ion mobility or mass transport is facilitated. Furthermore, some materials beyond graphene, e.g., layered double hydroxides (LDH), possess improved electronic conductivity at ultrathin features as in the case of atomic-thickness nanosheets.⁸ And the exploration of nanometer thick 2D crystals with intriguing physical and chemical properties has effectively expanded the family of 2D materials.⁹⁻¹⁰

Notably, the unique structural and electronic properties of 2D materials have prompted intense exploration in search for catalysis.¹⁰ The successful preparation of various 2D crystals¹¹ has nurtured the diversity of heterostructures that could be derived, where the synergetic effect plays a pivotal role in optimizing the kinetics and energetics of surface catalysis.⁶,¹² Aiming at improving performance, frontiers of 2D materials such as graphene, graphitic carbon nitride (g-C₃N₄), transition metal dichalcogenides (TMDs) have been integrated with other materials. The merits resulting from synergism of the constituent components and the fascinating properties at the interface are tremendously interesting.⁶,¹³ This scenario has now become the state-of-the-art point in the development of active catalysts for assisting energy conversion reactions including water splitting and CO₂ reduction. Hence, the construction of heterostructures has gone through considerable advances deserving a comprehensive outlook and plausible forecasts. Herein, after introducing frontier 2D materials, we trace the progressive developments in the design and applications of their heterostructures. Particular emphasis will be given to the efforts for developing efficient catalysts to drive important, yet thermodynamically challenging, reactions. Finally, we offer our perspective on the exploration of 2D heterostructures for further potential application in catalysis.

1.1. Graphene

Graphene is characterized by a single-atom-thick nanosheet of planar structure (Figure 1a) in which sp²-hybridized carbon atoms are arranged in a honeycomb lattice imparting excellent
conductivity and extraordinary mechanical and chemical stability. In the case where a heterostructure photocatalyst is designed making graphene as one of the components, a rapid electron transfer from the catalyst to graphene can be achieved as the Fermi level of graphene (0 V vs NHE) is lower than the conduction band position of most photocatalysts. This ensures a high spatial separation of the photogenerated electron–hole pairs due to the rapidly transferring of electrons from photocatalyst, whereas those of holes left for oxidation purpose, to graphene. The ultralarge theoretical surface area (2630 m² g⁻¹) of graphene is also another feature. This can be associated with the increase of surface active sites which is quite beneficial for catalysis. The case of CO₂ reduction takes particular advantages from the graphene’s large 2D π-conjugated structure, well consistent with the π-conjugated bond in CO₂ molecular. The initiation of a π–π conjugation interaction between graphene and CO₂ remarkably contributes to the adsorption of CO₂ molecules on the surface of graphene containing catalysts and eventually easing their reduction. Another intriguing feature that currently won the attention is the possibility of atomic dispersion in the graphene matrix. This is practically obvious for reduced graphene oxide (rGO) that develops a large volume of surface functional groups that would serve as anchoring sites and prevent aggregation. Thus, various metal atoms, e.g., Ni, Co, etc., can be uniformly deposited on the surface of graphene or rGO nanosheets with atomic dispersion. The single-atom implantation on the 2D surface could realize excellent catalytic activity in CO₂ reduction and hydrogen evolution reaction (HER). This conveys the current status of this field that has now reached the level of tenaciously implanting single metal atom in 2D materials for superior activity.

1.2. Graphitic Carbon Nitride

The metal-free polymeric material known as g-C₃N₄ is perhaps one of the oldest 2D framework in the record of scientific literatures. Its history goes back to the identification of melon, linear polymer consisting of interconnected tri-s-triazines via secondary nitrogen, in the 1830s (Figure 1b). In the case of g-C₃N₄, the arrangement appears in the 2D form in which the atoms are composed of tri-s-triazines interconnected via tertiary amines. There exists a close resemblance in terms of π-conjugation and 2D feature with that of graphite as has been proven experimentally. The altered localization of electrons and the presence of nitrogen atoms are thought to be the reason behind the smaller interlayer distance (0.326 nm) in g-C₃N₄ than that in graphite (0.335 nm). The most intriguing feature of g-C₃N₄ relies on the s-triazine ring structure. It shows a considerable thermal (up to 600 °C in air) and chemical resistance (stable in acids, alkalis, and various organic solvents). Unlike graphene, g-C₃N₄ possesses an appealing electronic structure with suitable bandgap for harvesting solar energy in a wider spectrum. The history of 2D g-C₃N₄ in heterogeneous catalysis is rather very recent. It has been recognized as a metal-free visible-light-driven photocatalyst for hydrogen production from water in 2009. This material is significantly robust and nonvolatile because its oxidation and reduction potentials are energetically suitable for water splitting. It is also possible to entrap metal or other functional materials to expose active sites with abundant melon moieties in the framework. It...
is predictable that combining g-C$_3$N$_4$ with other 2D materials, e.g., MoS$_2$, NiFe-LDH, etc., will induce unique electronic, mechanical, and chemical properties tunable with respect to efficiently catalyzing the desired reaction. This results in a tremendous amount of interest to construct active and stable catalysts.

1.3. Transition Metal Dichalcogenides

Transition metal dichalcogenides are other class of 2D materials that are vastly investigated following the unconventional properties of graphene. TMDs have attracted significant interests due to their promising energy applications and striking fundamental properties. The typical crystal structure is illustrated in Figure 1c. In their layered structure, each unit is composed of a transition metal (M) layer sandwiched between two chalcogen (X) atomic layers. Depending on the particular combination of transition metal and chalcogen elements, TMDs can have thermodynamically stable phase of either 2H or 1T phase, and other phases can be obtained as a metastable. The atoms are covalently bonded within each layer (X–M–X), where the metal and chalcogen atoms have oxidation states of $+4$ and $-2$, respectively. And the individual layers are connected together by weak van der Waals (vdW) forces. The surface of the layers is terminated by the lone pair of chalcogen atoms. As a result of the difference in oxidation states, considerable ionic character is induced between the metal and chalcogen atoms. Moreover, the 2D TMD nanosheets could be achieved by exfoliation of bulk crystals or building up individual atoms via vapor deposition. These situations pave the way leading to maximal exposure of active sites for catalysis. The unique structure of TMDs can also be visualized from the perspectives of two distinctive orientation featured by surface inertness (basal planes) and high surface energy (edges) exhibiting anisotropic properties. It has been observed that the electrical conductivity along the layer is ~2200 times higher than that across the vdW gaps between layers, predicting a considerably faster electron transport on the edges as compared to the basal planes. Such inherent characteristic of TMDs can give rise to a prominently active catalysis in electrocatalytic hydrogen evolution reaction provided that the active edges is maximally exposed. Therefore, increasing the conductivity and improving the density of accessible edges of TMDs have been proposed in the past few years as a means of attaining enhanced performances. Heterostructurring plays a pivotal role in tuning the catalytic activities of TMDs.

1.4. Others

Many other 2D layered materials, such as transition metal carbonitrides (MXenes), layered double hydroxides, metal–organic frameworks (MOFs), etc., are designed and synthesized. These basic crystal structure are used as catalysts for given reactions. As to MXenes, they are widely utilized as active materials in energy conversion. Some of them are explored for catalyzing water splitting. For example, Mo$_2$CT was theoretically and experimentally studied by She et al. for stable HER activity in acid media. It possessed a small hydrogen absorption energy of 0.048 eV. They speculated that the basal planes of Mo$_2$CT are catalytically active toward HER, which is different with the case in hexagonal phased MoS$_2$.

2. Heterostructures Based on 2D materials

This extensive library of layered 2D materials provides the possibility to design heterogeneous integration for novel hybrid structures. The dangling-bond-free surface is demonstrated...
on each layer of 2D crystal without direct chemical bonding to the adjacent layer. The interaction between the neighboring layers of these layered materials are characterized by van der Waals force. Thus, the highly disparate materials could be integrated without constricts of crystal lattice mismatching. In this regard, theoretical models are widely applied to understand the properties of various 2D crystals and their heterostructures. The electronic and elastic properties of 2D mono/heterostructures are predicted through many theoretical approaches, like ab initio and tight-binding (TB) methods.[40] The excellent properties of 2D materials are even more pronounced when they are integrated with other functional materials to construct 2D–2D, 1D–2D, and 2D–0D heterostructures, as exemplified in Figure 1d–f. Being able to incorporate multiple electronic features into one system, the design of heterostructures has brought us versatile functionalities. The structural and electronic benefit of heterostructures formation provide a fertile ground to maximize the geometrical exposure of active edge sites and optimize the energetics and kinetics of catalytic reactions. Particularly, the merits resulting from synergism of the constituent components and the fascinating properties at the interface are tremendously interesting. It is believed that heterostructures formed by combination of two different materials play important role in catalytic reactions as “a combined-two is better than an isolated-two.”[41] When heterostructures form, there would be variation in the work function, the position of the valence band and conduction band, and the density of states.[42] These variations lead to entirely different electronic structures thereby endowing a great opportunity in tuning the carrier distribution and mobility for enhanced activity.

2.1. Structural and Electronic Properties

The heterostructures, potentially integrating the advantages and overcoming the weakness of the individual ones, usually consist of two or more distinctive components. The rational construction of the heterostructure could tune the electronic structure to realize the efficient catalytic activity due to a synergistic effect between the different components.[43] When contacting different crystals together, charge redistribution or strain might occur between the neighboring crystals. Thus, the change of the properties, including electronic and structural ones, will be induced in each other.[44]

The heterostructure based on 2D materials can be generally classified as lateral heterostructure and vertical heterostructure (Figure 2a,b). The lateral heterostructure are constructed with different 2D crystals, which are bonded in atomic level.[43,45] The chemical vapor phase epitaxial growth method[46] is utilized to construct the ternary or multivariate ordered heterostructures on lateral direction. With this method, the graphene-h-BN[47] and various TMD (i.e., MoS 2, WS 2, and MoTe 2) based heterostructures[48] in one plane have been realized recently. Park and co-workers[49] synthesized coherent atomically thin superlattices where WS 2 and WSe 2 monolayers are repeated and laterally integrated within the single layer (Figure 2c). These dislocation-free superlattices fully matched lattice constant across heterointerfaces with an isotropic lattice structure and triangular symmetry. Figure 2d shows the structural information with the orientation of a perpendicular to the heterointerfaces, provided by the electron microscope pixel array detector (EMPAD), of the whole superlattices with nanoscale resolution, revealing the lattice coherence. Furthermore, the
selective-area electron diffraction (SAED) data (Figure 2e) exhibited a single-crystal-like pattern with sharp and isotropic diffraction spots. A single diffraction spot with no separation on // (parallel to the heterointerfaces) orientation confirms the perfect lattice matching. And similar lattice constants were also observed in the diffraction data corresponding to ⊥ (Figure 2f).

Such coherent superlattices with strain will endow the lateral heterostructures with targeted functionalities, including catalytic activity. Additionally, vertical heterostructures (Figure 2b) with one crystalline 2D crystal on the top of another one are widely studied. Graphene, as an excellent conductor, has been used to support other 2D nanosheets, such as topological insulators \[(i.e., \text{Bi}_2\text{Se}_3, \text{In}_2\text{Se}_3)\] semiconductors \[(i.e., \text{MoS}_2)\] and metals \[(i.e., \text{MoC}_2)\]. In the past few years, a variety of TMD heterostructures have been prepared via epitaxial growth methods \[(54,55)\] and combinatorial technologies (exfoliation and restacking). \[(56)\]

Latest, different with the previous methods, an electrochemical molecular intercalation approach was explored by Wang et al. \[(57)\] to fabricate stable superlattices in vertical direction. As seen in Figure 2g, intercalation with cetyl-trimethylammonium bromide (CTAB) in the vander Waals interlayers of black phosphorus (BP) could produce monolayer phosphorene molecular superlattices. Compared with the interlayer distance of BP (5.24 Å), that of new superlattice (Figure 2h–i) will be uniformly enlarged by two times (11.21 Å). Significantly, this approach provides an opportunity to construct a wide range of functional-molecular-modified superlattices with 2D materials as a versatile platform for physics studies or catalytic reactions. The similar heterostructure, consist of graphene oxide and titanium oxide, also designed through self-assembly. \[(58)\]

It is to be noted that the strong interlayer or interface coupling of charge carriers \[(59,60)\] will be introduced when the two crystals are brought together. In this case, the charge redistribution occurs on the interface and it will tune the electronic states. As shown in Figure 3a, \[(61)\] when connecting W\(_2\text{C}\) with WS\(_2\), an apparent electron of 0.12 |e| transfer from the W atoms of W\(_2\text{C}\) to WS\(_2\), and S atoms simultaneously gain more 0.16 |e|.

The density of state (DOS) spectra (Figure 3b) show that the electronic density is reduced around the Fermi level, suggesting the regulation of Gibbs free energy (\(\Delta G_{\text{H}}\)) for hydrogen adsorption on the interface and improvement of the hydrogen evolution activity at the interface. Many research groups \[(62–64)\] also found the fine control over the edge of TMD crystals between graphene or rGO sheets resulted in the high electrocatalytic activity in the hydrogen evolution reaction. Besides, the lattice mismatched or rotated heterostructures, especially the 2D–2D ones, will lead to the surface reconstruction. The occurrence of the Moire pattern on the vertical heterostructure verify the spatially varying interlayer coupling strength and electrostatic potential. \[(65,66)\] Figure 3c shows the calculated valence-band
maximum (VBM) state and conduction band minimum (CBM) state of MoSe₂/MoS₂ heterostructure. The VBM state is predicted to be strongly localized, while CBM state is weakly localized. Such wave function localization were found in many 2D vdW heterostructures. As demonstrated in Figure 3d, a Moire pattern of vertical WSe₂/MoS₂ heterostructure was clearly visible in the high-resolution transmission electron microscopy (HRTEM) image. This localized state and charge transfer across the atomic planes would have major impacts on the carrier migration, electronic and chemical reactivity on the surface. For the lateral heterostructure, such as C₆₀/C₆₀, plane heterostructural nanosheet, this unique plane could synchronously accelerate electron–hole pair separation and electron transport via in-plane π-conjugated electric field for efficient photocatalytic water splitting (Figure 3e). And this configuration is also fabricated to promote the electrochemically overall water splitting.

Another intriguing effect can be realized by combining two semiconducting crystals. The carrier delocalization will be induced by the sufficient hybridization, resulting in band bending and formation of a built-in potential, of atomic orbitals due to the strongly bonded interface. This structure is particularly promising for photocatalysis. Based on their band alignments, heterostructures contain three types, namely, type I, type II, and type III, which are displayed in Figure 3f. Each of these band alignments are utilized in specific system. For instance, the type I band alignments and type III are widely used in optical devices (light-emitting diodes (1)) and tunneling field effect transistors (5). Type II band alignments are very useful for solar cells (3), photocatalysis ((3) and (4)) or electronic devices (2). But, when constructing the type II heterostructure for photocatalytic water splitting, the redox potentials of pure water (Figure 3g) should be carefully considered.

The following section deals with the prominent applications of 2D materials based heterostructures in catalysis. It is obvious one can see a remarkable enhancement in the case of heterostructures of optimized components as compared to either of the single components for the reason mentioned above.

3. Promising Applications in Catalysis

The performance of a given catalyst depends on the effort of exposing active sites on the surface. Table 1 summarizes the recent reports about heterostructures containing 2D materials. It can be envisioned that the catalytic activity, especially in hydrogen evolution reaction through water splitting and CO₂ reduction for value added organic compounds, significantly improves for the heterostructures built from optimized components as compared to their single component counterparts. Notably, compared with the other hybrid materials, the high-quality interfaces between 2D nanocrystal and other functional materials in 2D heterostructures could provide ideally aligned band offsets, which is essential for photocatalysis. Due to the 2D feature of these materials, tuning of electronic structure, closely related to electrocatalysis, can easily be realized via regulating the concentration of defects or strain. As such, the design of 2D materials finds a promising way for excellent performance in activity, stability, and selectivity toward a given reaction and used in industrial catalysis instead of noble metal catalysts. The 2D catalysts should also be built from elementally abundant and less expensive materials for a widespread application. Maximal exposure of active sites based on entirely earth-abundant elements with controllability and large-area uniformity is an essential requirement for practical applications. Up to know, solution processes are widely utilized to synthesize the 2D heterostructures with large-scale production. In order to fabricate the 2D heterostructure with high-quality interface, the chemical vapor deposition method is preferred. However, the large-scale production of 2D catalysts by this method is defective and challenging. Much more efforts should be made in this direction. The structural and electronic benefits of heterostructures provide a fertile ground to maximize the geometrical exposure of active edge sites and optimize the energetics and kinetics of catalytic reactions.

3.1. Water Splitting

The construction of various kinds of heterostructures based on 2D materials offers great opportunities for boosting the catalytic performance in both electrocatalysis and photocatalysis of water splitting reactions. Apart from introducing defects and dislocations, there will be charge transfer process across the interface as mentioned in Section 2.1. The induced charge distribution between the components, forming up the heterostructure, plays a key role in hydrogen atom adsorption and desorption kinetics. This remarkably reduces the overpotential required to derive electrocatalytic water splitting reactions. Given these merits, the semiconducting MoS₂ nanosheet is coupled with the most conductive graphene via different synthesis methods (Table 1) and junction types in the quest for enhanced performance. The work by Dai and co-workers is a typical example representing a 0D–2D heterostructure between MoS₂ and reduced graphene oxide. MoS₂ nanoparticles can be selectively grown on the surface of graphene oxide (GO) as a result of the interaction between the functional groups of GO sheet and the precursor used as a source of Mo. An appropriate solvent is required for this to achieve a well-dispersed 0D–2D heterostructure. Owing to the rapid electron transfer across the underlying MoS₂–rGO network and creation of abundant active sites, this hybrid structure exhibits improved HER activity in acid solution as compared to either of the single components (MoS₂ nanoparticles or rGO). It has, recently, been observed that graphene-mediated charge-transfer kinetics can result in synergizing the 2D–2D heterostructure between Mo₂C and graphene. With the optimized reaction time and CH₄ flow rate in chemical vapor deposition (CVD) operation, the controllable nucleation of Mo₂C flakes on graphene sheet has been observed as depicted in Figure 4a. In due course of the reaction, Mo₂C flakes first nucleate on already formed graphene sheet. As the reaction time increases, further nucleation of Mo₂C flakes takes place which eventually coalesce into a continuous film. Figure 4b demonstrates the enhanced HER activity of the heterostructure which can be attributable to the high crystallinity of the Mo₂C flakes and the excellent electronic coupling to graphene, collectively contributing to rapid charge transfer kinetics for H₂ adsorption and H₂ molecule desorption. Considering the practical application, the relatively low current density values, around tens of mA per square
**Table 1. Summary of recent reports about 2D-based heterostructures for catalyzing various reactions.**

| Heterostructures | Type of junction | Synthesis methods | Structural features | Unique properties | Applications | Performance | Ref. |
|-------------------|------------------|-------------------|--------------------|------------------|--------------|-------------|------|
| MoS\textsubscript{2}-hydrogenated graphene | 2D–2D | Solvothermal | Ultrathin MoS\textsubscript{2} nanosheets grown on hydrogenated graphene | structural and electronic modulations | HER | η\textsubscript{10} = 124 mV, Tafel slope = 41 mV decade\textsuperscript{-1}, TOF\textsubscript{200mV} = 7.8 s\textsuperscript{-1} | [98] |
| MoS\textsubscript{2}-graphene | 0D–2D | Hydrothermal reaction of (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} with hydrazine in DMF solution containing mesoporous graphene foam as the matrix | Well-dispersed and ultrafine MoS\textsubscript{2} nanoparticles (≈2 nm) were grown on the graphene | – Abundance of catalytic edge sites, – The increase in electrochemically accessible surface area – The unique synergetic effects between the graphene and MoS\textsubscript{2} | HER | η\textsubscript{10} = 200 mV, onset = 100 mV, Tafel slope = 42 mV decade\textsuperscript{-1}, | [99] |
| MoS\textsubscript{2}–rGO | 2D–2D | Intercalation via solvent evaporation | Layer confined structure of MoS\textsubscript{2}–rGO | oxidation degree of graphene, the crystallinity of MoS\textsubscript{2} and the exposed active site affect the catalytic activity | HER | η\textsubscript{10} = 200 mV, onset = 140 mV, Tafel slope = 41 mV decade\textsuperscript{-1}, | [100] |
| MoS\textsubscript{2}–rGO | 0D–2D | Solvothermal synthesis of MoS\textsubscript{2} nanoparticles on rGO sheets suspended in solution | Few-layer and nonaggregated MoS\textsubscript{2} structures with an abundance of exposed edges stacked onto graphene sheet | strong chemical and electronic coupling between the GO sheets and MoS\textsubscript{2} | HER | onset = 100 mV, Tafel slope = 41 mV decade\textsuperscript{-1}, | [62] |
| MoS\textsubscript{2}–rGO | 2D–2D | Sonication, followed by solvothermal | MoS\textsubscript{2} nanosheets grown on the rGO sheets | confined growth of MoS\textsubscript{2} on the GO sheets results in rich active edges and improved electrical conductivity | HER | onset = 0.13 V, η\textsubscript{10} = 218 mV, Tafel slope = 57 mV decade\textsuperscript{-1}, | [101] |
| MoS\textsubscript{2}–N-doped graphene | 2D–2D | Vacuum-assisted filtration followed by electrodeposition | Amorphous MoS\textsubscript{2}, matrix electrodeposited on graphene to give hydrated 3D framework | The hydrogel framework in the composite structure enhances the electrode wettability and facilitates the access to electrolytes | HER | η\textsubscript{10} = 140.6 mV, Tafel slope = 105 mV decade\textsuperscript{-1}, | [102] |
| Cu–MoS\textsubscript{2}–rGO | 2D–2D | Sonication followed by solvothermal | MoS\textsubscript{2} nanoflowers with crumpled nanosheets dispersed on 2D graphene | – Plenty of folded edges exposed – rGO improved the electrical conductivity of the catalyst | HER | onset = 126 mV, η\textsubscript{10} = 400 mV, Tafel slope = 90 mV decade\textsuperscript{-1}, | [103] |
| rGO–WS\textsubscript{2} | 2D–2D | Hydrothermal, CVD, sensitization | rGO nanosheets dispersed on the surface of vertically oriented WS\textsubscript{2} nanosheets | synergism from the decoration by rGO through a remarkable area of contact on WS\textsubscript{2} surface that enhanced the electron transport phenomena | HER | η\textsubscript{10} = 229 mV, Tafel slope = 73 mV decade\textsuperscript{-1}, | [63] |
| MoS\textsubscript{2}–CNT | 2D–1D | Solvothermal | 1D network coated by sheet-like subunit | The presence of CNTs in the composite leads to rapid electron transport from the less conducting MoS\textsubscript{2} nanosheets to the electrode | HER | onset = 0.09 V, Tafel slope = 44.6 mV decade\textsuperscript{-1}, TOF\textsubscript{0mV} = 0.06 s\textsuperscript{-1} | [104] |
| MoS\textsubscript{2}–N-doped CNT | 2D–1D | Plasma-enhanced chemical vapor deposition followed by thiomolybdate decomposition | Amorphous molybdenum sulfide (MoS\textsubscript{2}) layer directly bound at vertical N-doped carbon nanotube (NCNT) forest surface | Excellent HER catalysis due to synergism and rapid charge transport along NCNT forest | HER | onset = 75 mV, η\textsubscript{10} = 110 mV, Tafel slope = 40 mV decade\textsuperscript{-1}, TOF\textsubscript{200mV} = 3.3 s\textsuperscript{-1}, | [105] |
| MoS\textsubscript{2}–C nanosheet | 2D–2D | Microemulsion procedure | Defect rich hierarchical spheres in which MoS\textsubscript{2} nanosheets grew outwards from the inner core | The S ions produced from CS\textsubscript{2} diffused into the aqueous phase and multiple Mo ions competed in reaction with the same S ion, forming Mo–S–Mo compounds with more S defects | HER | onset = 103 mV, η\textsubscript{10} = 159 mV, Tafel slope = 57 mV decade\textsuperscript{-1}, | [106] |
| Heterostructures          | Type of junction | Synthesis methods                                                                 | Structural features                                                                                                           | Unique properties                                                                                                           | Applications                          | Performance                                                                 | Ref.    |
|---------------------------|------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|---------------------------------------|----------------------------------------------------------------------------|---------|
| Mo₂C–graphene             | 2D–2D            | Catalyst-assisted CVD                                                             | Centimeter range Mo₂C hexagonal film grown on in situ formed graphene                                                      | Enhanced charge transfer kinetic across the interface                                                                      | HER                                  | HER onset = 87 mV, η₁₀ = 236 mV, Tafel slope = 73 mV decade⁻¹               | [74]    |
| MoO₂–MoS₂                 | 0D–2D            | Hydrothermal method followed by sulfurization by H₂S                              | MoS₂ sheets contour the surface of most of the MoO₂ crystals                                                                | MoO₂ surface can sulfide by inward progression of MoO₂(20-2)/MoS₂(002) interfaces resulting in upright-oriented and edge exposing MoS₂ sheets | –                                    | –                                                                          | [107]  |
| MoO₂–MoSe₂                | 2D core–shell    | CVD method followed by calcination under Se atmosphere                             | Trapezoid-like MoO₂/MoS₂ core–shell nanosheets grown on the substrate                                                         | High crystalline mismatch between MoO₂ and MoSe₂ provides defects and dislocations                                         | HER                                  | HER onset = 63 mV, η₁₀ = 181 mV, Tafel slope = 49.1 mV decade⁻¹            | [108]  |
| ZnIn₂S₄–MoS₂–rGO          | 0D–2D            | Hydrothermal                                                                      | ZnIn₂S₄ nanosheets uniformly dispersed on MoS₂–rGO nanosheet without aggregation                                             | Efficient interface transfer of photoinduced electrons and holes from g-C₃N₄ to ZnIn₂S₄ nanosheets                           | Photo. HER                           | H₂ evolution rate = 425.1 µmol h⁻¹ g⁻¹                                     | [109]  |
| Co₃O₄@C–N nanosheet arrays| 0D–2D            | Electrodeposition, CVD                                                            | Co₃O₄ NPs uniformly anchored on s p²-hybridized carbon–nitrogen nanosheet array                                              | The Co₃O₄ NPs uniformly anchored on the nanosheet array brings about more active sites, boosting mass transport and electron transfer | OER                                  | η₁₀ = 245 mV, Tafel slope = 65 mV decade⁻¹, TOF₃⁰₅₀mV = 0.958 s⁻¹         | [112]  |
| CoNi–LDH–CoO              | 2D–0D            | in situ reduction and interface-directed assembly                                   | 2D nanosheets with randomly cross-linked CoNi layered double hydroxide and small CoO nanocrystals                         | These unique characteristics result in a high-density active sites, improving the affinity between OH⁻ and catalyst, and resulting in a large accessible surface area and permeable channels for ion adsorption and transport | OER                                  | η₁₀ = 1.48 V, Tafel slope = 123 mV decade⁻¹, TOF₃⁰₅₀mV = 1.4 s⁻¹            | [113]  |
| NiPS₃ nanosheet–graphene  | 2D–2D            | Sonication                                                                        | The small NiPS₃ nanosheets uniformly attached on the basal planes of large graphene sheets                                 | The greatly increased active surface areas and significantly decreased electron transfer resistance caused by the synergistic effect | OER                                  | η₁₀ = 1.48 V, Tafel slope = 42.6 mV decade⁻¹, TOF₃⁰₅₀mV = 0.0249 s⁻¹       | [114]  |
| FeNi–LDH/Ti₃Cₓ–MXene      | 2D–2D            | Centrifugation, freeze-drying                                                     | Ionic heteroassembly of interconnected porous network of FeNi–LDH nanoplates on Ti₃Cₓ MXene nanosheets                          | Prominent charge transfer from LDH to MXene is identified to accelerate the redox process                                    | OER                                  | η₁₀ = 298 mV, Tafel slope = 43 mV decade⁻¹, TOF₃⁰₅₀mV = 0.26 s⁻¹        | [115]  |
| Heterostructures     | Type of junction | Synthesis methods                        | Structural features                                                                 | Unique properties                                                                 | Applications                                           | Performance                                      | Ref. |
|----------------------|------------------|------------------------------------------|-------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------|--------------------------------------------------|------|
| CdS–MoS₂             | 1D–2D            | Glucose-assisted hydrothermal            | MoS₂ nanosheets oriented vertically on CdS nanowire                                 | High exposure of the active edge sites and increased charge separation and transfer rate | Photo. HER                                            | H₂ evolution rate = 9.73 mmol h⁻¹ g⁻¹             | [116]|
| MoS₂–graphene–TiO₂   | 0D–2D–2D         | Hydrothermal                             | TiO₂ nanoparticles grown on layered MoS₂–graphene hybrid sheet                      | MoS₂ nanosheets on graphene sheets accept electrons from the CB of TiO₂ and facilitate hydrogen production | Photo. HER                                            | H₂ evolution rate = 165.3 µmol h⁻¹               | [81] |
| MoS₂–rGO             | 2D–3D            | CVD and Hammer’s method                  | Heterojunctions composed of 3D nanoporous reduced graphene oxide as visible light absorber and 2D monolayer MoS₂ as active catalyst | The built-in electric field created by space charge of the heterojunction suppresses the electron–hole recombination and promotes the formation of electron-rich MoS₂ for increased HER | Photo. HER                                            | onset = 48 mV, η₅₀ = 141 mV, Tafel slope = 61 mV decade⁻¹ | [117]|
| MoS₂–g-C₃N₄          | 0D–2D            | Hydrothermal                             | MoS₂ quantum dots dispersed uniformly on the surface of g-C₃N₄                        | The heterojunction promotes the separation of photoinduced charge carriers and enhance water splitting reaction | Photo. HER                                            | H₂ evolution rate = 1.42 mmol h⁻¹ g⁻¹             | [118]|
| MoS₂/WS₂, WS₂/MoS₂    | 2D–2D            | A two-step CVD method                    | Well-defined triangular sheets of WS₂ or (MoS₂) are uniformly deposited on monolayer MoS₂/Au (or WS₂/Au) | Effective electron–hole separation and fast electron transfer kinetics assisted by Type-II band alignment | Photo. HER                                            | H₂ evolution rate = 1.819 µmol h⁻¹ cm⁻²           | [54] |
| MoS₂/g-C₃N₄/GO        | 0D–0D–2D         | Hummers’ method, sonication, condensation polymerization | Quantum dots of C₃N₄ and MoS₂ are dispersed with slight aggregation on the surface of graphene oxide sheet | Energy bands are aligned such that the collection of electrons are in MoS₂ and holes are in g-C₃N₄ | Photo. HER                                            | H₂ evolution rate = 1.65 mmol h⁻¹ g⁻¹             | [82] |
| Zn₀.₈Cd₀.₂S–rGO (ₓ = 0.8) | 0D–2D         | Coprecipitation–hydrothermal             | Nanoparticles of ZnₓCdₙ₋ₓS dispersed on the surface of rGO sheet                    | rGO serves as electron collector and transporter – the photoinduced electrons in CB of Zn₀.₈Cd₀.₂S tend to transfer to rGO, leading to enhanced charge carrier separation | Photo. HER                                            | H₂ evolution rate = 1.824 µmol h⁻¹ g⁻¹             | [119]|
| g-C₃N₄–MoS₂           | 2D–2D            | Impregnation of mesoporous carbon nitride with an aqueous solution of (NH₄)₂MoS₄, followed by sulfuration | Slabs of MoS₂ deposited on the surface of mesoporous carbon nitride sheet and form a thin junction | The intimate thin junction ensures short carrier transport distance owing to the electron-tunneling effect through MoS₂ thin layers to reaction interfaces | Photo. HER                                            | H₂ evolution rate = 20.6 µmol h⁻¹                 | [28] |
| Cds–WS₂–g-C₃N₄        | 2D–2D            | Hydrothermal, exfoliation, chemical impregnation method | WS₂ nanosheets were anchored on the surface of CN to form an intimate junction | Efficient charge-transfer pathways accelerate the separation and migration of photoinduced electrons and holes | Photo. HER                                            | H₂ evolution rate = 1174.5 µmol h⁻¹ g⁻¹           | [120]|
| Phosphorene–g-C₃N₄    | 2D–2D            | Self-assembly via physical mixing        | The g-C₃N₄ nanosheets are deposited on the surface of phosphorene nanosheet           | Intimate electronic coupling between the components contributes to enhanced charge separation | Photo. HER                                            | H₂ evolution rate = 571 µmol h⁻¹ g⁻¹              | [121]|

### Table 1. Continued.
| Heterostructures       | Type of junction | Synthesis methods                       | Structural features                                      | Unique properties                                                                                     | Applications                  | Performance                        | Ref. |
|------------------------|------------------|-----------------------------------------|----------------------------------------------------------|-------------------------------------------------------------------------------------------------------|-------------------------------|-----------------------------------|------|
| g-C3N4–Cring           | Lateral 2D–2D    | Hydrothermal conjugation                | Sheet-like \(\text{Cring})\–g-C3N4 homogeneously connected without the growth of nanoparticles. | Improved charge carrier separation and fast spatial transport of photoinduced electrons assisted by in-plane \(\pi\)-conjugated electric field | Photo-water splitting          | \(H_2\) evolution rate = 371 \(\mu\)mol h\(^{-1}\) g\(^{-1}\) | [67] |
| g-C3N4–NiAl–LDH        | 2D–2D            | Thermal condensation, exfoliation, hydrothermal | Ultrathin 2D LDH sheets grown on g-C3N4                    | Electrostatic self-assembly between positively charged NiAl–LDH sheets and negatively charged g-C3N4 nanosheets form an intimate interface promoting fast electron transfer | Photo-CO\(_2\) red.            | CO evolution rate = 8.2 \(\mu\)mol h\(^{-1}\) g\(^{-1}\) | [122]|
| rGO–CdS                | 2D–1D            | Microwave-assisted hydrothermal         | CdS nanorods dispersed on rGO sheets                      | The 1D CdS nanorod act as electron acceptor and transporter, The rGO facilitates the CO\(_2\) adsorption and activation | Photo-CO\(_2\) red.            | CH\(_4\) evolution rate = 2.51 \(\mu\)mol h\(^{-1}\) g\(^{-1}\) | [87] |
| Cu–graphene oxide      | 0D–2D            | Microwave heating                       | Cu nanoparticles dispersed on the surface of few layered graphene oxide sheet | Suppression of electron-hole pair recombination, Narrowing of the graphene oxide’s bandgap, and modification of its work function | Photo-CO\(_2\) red.            | Solar fuel formation rate = 6.84 \(\mu\)mol g\(_{\text{cat}}\) h\(^{-1}\) | [93] |
| TiO\(_2\)–graphene–MoS\(_2\) | 2D–2D            | Hammers method, hydrothermal method     | 2D rGO sheets assembled into macroporous 3D structures on to which TiO\(_2\) nanoparticles and MoS\(_2\) nanosheets are uniformly distributed | The electron flow from TiO\(_2\) via graphene into the few-layered MoS\(_2\) could effectively lower the charge recombination rate and increase the potential for CO\(_2\) reduction | Photo-CO\(_2\) red.            | CO evolution rate = 92.33 \(\mu\)mol g\(^{-1}\) h\(^{-1}\) | [123]|
| g-C3N4–rGO             | 2D–2D            | Thermal polymerization, exfoliation, Hammers’ method | Sheet on sheet like structure was formed via surface electrostatic interaction between negatively charged GO and positively charged carbon nitride | The heterojunction promotes the separation of electron hole pairs | Photo-CO\(_2\) red.            | CH\(_4\) evolution = 13.93 \(\mu\)mol g\(^{-1}\) | [88] |
| g-C3N4–Fe\(_2\)O\(_3\) | 2D–3D            | Hydrothermal, impregnation              | Hierarchical Z-scheme heterojunction with urchin-like nanosheets | The Fe\(_2\)O\(_3\) promotes CO\(_2\) adsorption and the Z-scheme feature increase the lifetime of separated charge carriers | Photo-CO\(_2\) red.            | CO evolution rate = 27.2 \(\mu\)mol g\(_{\text{cat}}\) h\(^{-1}\) | [90] |
| Single-atom Co-partially oxidized graphene | 0D–2D | Sonication, freeze drying | Isolated Co atoms are randomly dispersed on the graphene sheet | The isolated Co atoms act as active sites, the graphene network bridges the light absorber and the active sites | Photo-CO\(_2\) red.            | CO Selectivity = 79.4% TOF = 3.77 min\(^{-1}\) | [18] |
| Single Ni-atom–N-doped graphene | 0D–2D | Pyrolysis at high temperature, sonication, hydrothermal | Ni species are dispersed as single atoms on the graphene sheets | The low-valent (I) Ni atomic center having electronic configuration act as active site to reduce CO\(_2\) | Electrocat CO\(_2\) red. | Faradaic efficiency = 97% TOF\(_{0.61\text{V}}\) = 14 800 h\(^{-1}\) | [20] |
| Single Ni-atom in graphene | 0D–2D | Impregnation and reduction | The large area, negatively charged surface helped in uniformly adsorbing a monolayer of positive metal cations for single-atom dispersion | Ni single-atomic sites have high selectivity for CO production | Electrocat CO\(_2\) red. | CO selectivity\(_{550\text{mV}}\) = 95% TOF\(_{550\text{mV}}\) = 6.8 s\(^{-1}\) | [95] |
| Table 1. Continued.                                                                 |                                                                                                               |                                                                                                              |                                                                                                      |                                                                                         |                                                                                           |      |
centimeter, and high overpotential of these 2D heterostructured HER catalysts is a substantial challenge. Thus, exploring the efficient electrocatalysts with 2D heterostructures is critical in the future studies.

As the anodic reaction of water splitting, oxygen evolution reaction (OER) is sluggish due to involving four electrons. Some OER electrocatalysts based on 2D heterostructures are also designed for decreasing the overpotential to generate oxygen gas through splitting water. Yu and co-workers fabricated the in-plane black phosphorus/Co$_2$P heterostructure for electrocatalytic water splitting in alkaline media (1.0 M KOH). The high oxygen evolution activity is also realized using BP/Co$_2$P heterostructure. Besides, the vertical 2D heterostructures, such as Ni$_3$FeN/NRGO, were designed for improving OER performance. The strong coupling between Ni$_3$FeN nanoplates and graphene support tuned the electronic structure, critical for reaction steps, of the catalyst. To be noted, the OER activity using some of 2D materials, including chalcogenides and phosphides, is controversial due to the easy oxidation of these materials under the oxygen evolution condition. The confirmation and detection of their active sites via some in situ techniques for OER are essential in the following research.

In the case of photocatalysis, the issue of band alignment comes into play apart from the advantages mentioned for electrocatalysis. The special and commonly known structure called “Type-II junction” (Section 2.1) is widely acknowledged for elongating the lifetime of charge carriers via suppressing electron–hole recombination for different kinds of heterostructure. It obvious that plethora of reports have been made in attempt to boost the photocatalytic performance of TiO$_2$ since its first observation by Fujishima and Honda. The synergetic effect between MoS$_2$ and graphene in cocatalyzing HER on the surface of TiO$_2$ can be considered as one of the efforts. This heterostructure has two prominent advantages: i) graphene has high electron mobility, and hence the electrons on the conduction band (CB) of TiO$_2$ can be injected to the graphene sheet and experience accelerated kinetics; ii) the MoS$_2$ nanosheets that are dispersed on the graphene sheet can accept electrons and act as active sites for the photocatalysis. In different instances, graphene is frequently used as charge transport platform owing to its high carrier mobility. The ternary heterostructure built from MoS$_2$ quantum dots (QDs), g-C$_3$N$_4$ QDs, and graphene sheet results in junction system possessing improved interfacial contact between the QDs and the nanosheets along with the facilitated collection of electrons in MoS$_2$ and holes in g-C$_3$N$_4$. This configuration ensures charge separation and effectively suppress charge recombination (Figure 4c). The MoS$_2$ QDs are closely spaced with those of g-C$_3$N$_4$ which is intimately contacted with graphene, depicting the junctions of MoS$_2$ to g-C$_3$N$_4$ to graphene. Thus, such composite absorbs light in a wide range of spectrum and experiences high charge separation efficiency than the individual ones. This guarantees its improved performance in photocatalytic HER (Figure 4d). The nitrogen sites of g-C$_3$N$_4$ have lone pair of electrons which would confer an ideal platform for an intimate connection of components in heterostructures. This can be evidenced from...
the in-plane heterostructure built from g-C3N4 and C ring.\[67\] Such in-plane heterostructure illustrated in Figure 4e, having a pronounced \(\pi\)-conjugation, ensures enhanced photocarrier separation via swiftly trapping photoexcited electrons and driving them to suitable locations for catalysis. It is obvious from the HRTEM image in Figure 4f that the C ring (represented by orange colored elliptical shape) is randomly distributed on the basal plane of g-C3N4. There is remarkable amount of \(sp^2\)-hybridized electronic structure that avails more electrons around the Fermi level for suppressing charge carrier recombination and enhancing visible light absorption. As compared to the pristine g-C3N4, there is a 10 time increment in the photocatalytic hydrogen evolution rate for g-C3N4–C\(_{\text{ring}}\) heterostructure under visible light irradiation (Figure 4g).

The very recent report by Qiao and co-workers\[84\] reveals a metal-free heterojunction made via mechanical mixing of few layered phosphorene and g-C3N4 sheet (2D–2D). It behaves like a straddled type-I configuration wherein the photoinduced electrons in CB of g-C3N4 flow to the CB of phosphorene to do their job of catalysis. The strong electronic coupling, verified by the migration of electron from g-C3N4 to phosphorene, made an intact contact of g-C3N4 on the surface of few layered phosphorene. Phosphorene by itself does not have remarkable photocatalytic activity. The heterostructure endows a high interfacial charge transfer between these 2D components and a modification of the electronic structure. The 2D–2D heterojunction between phosphorene and g-C3N4 with optimized component ratio, could boost the photocatalytic HER performance considerably. Moreover, typical TMD materials, such as MoS\(_2\) and WS\(_2\) (as MoS\(_2\)/WS\(_2\) or WS\(_2\)/MoS\(_2\) depending on temperature of CVD reaction), have been brought to one another to give vertically oriented 2D–2D heterojunction on Au foil.\[54\] Distinct crystalline features can be substantiated in Figure 4h–i for WS\(_2\)/MoS\(_2\) and MoS\(_2\)/WS\(_2\), respectively. The white dashed line indicates the edge of the upper domain and the two fitted triangular lattices (in red and blue). Particularly, the vertically oriented MoS\(_2\)/WS\(_2\) behave like Type-II heterostructure ensuring elongated carrier lifetime and suppressed recombination rate. This can be validated from the enhanced photocatalytic hydrogen evolution rate observed for this sample in Figure 4j.

### 3.2. \(\text{CO}_2\) Reduction

The reduction of \(\text{CO}_2\) involves the breaking of the C=O bond and the formation of products such as carbon monoxide (CO), formate (\(\text{CHOO}\)), formaldehyde (HCHO), methanol (CH\(_2\)OH), methane (CH\(_4\)), ethanol (C\(_2\)H\(_5\)OH), etc. Unlike HER, the reduction of \(\text{CO}_2\) is challenging as it requires multistep reactions with more electron cost.\[85\] Moreover, the competitive reaction of HER can easily take off as a side reaction. This necessitates the design of catalysts with high selectivity that promote \(\text{CO}_2\) reduction and suppress HER. Heterostructure of 2D materials can be a promising platform. Particularly, graphene and g-C3N4 are acknowledged for being excellent support materials in photocatalyzing \(\text{CO}_2\) reduction; they maximize specific surface area and contribute to proliferation of active sites. Moreover, the interaction between graphene and \(\text{CO}_2\) takes a special advantage. There is also a delocalized \(\pi\)-\(\pi\) conjugation system in \(\text{CO}_2\) molecule. This \(\pi\)-\(\pi\) conjugation interaction between \(\text{CO}_2\) and graphene could ease \(\text{CO}_2\) adsorption and activation.\[86,87\] Ong et al.\[88\] have experimentally demonstrated this interaction using a 2D–2D hybrid structure obtained via \(\pi\)-\(\pi\) stacking and electrostatic attraction between rGO and g-C3N4 following protonation for surface charge modification. The SEM image in Figure 5a shows that “sheet on sheet” like structure, with distinct feature as revealed in the inset. At the interface of g-C3N4 and rGO, the photoexcited electrons at the CB of g-C3N4 percolate to the rGO sheet which has superior electron conductivity and high charge storage capacity. The high rate of \(\text{CH}_4\) (product of \(\text{CO}_2\) reduction) production, from optimum amount of components in the heterostructure, is attributable to this fact. As can be seen in Figure 5b, the performance of pure g-C3N4 is low due to the electron–hole recombination following its moderate bandgap. This is a common problem for single component photocatalysts. Using two different semiconductors, a configuration known as Z-scheme solves this problem via promoting the separation of the electron–hole pairs and enhancing the availability of electrons at CB in one of the semiconductors.\[89,90\] Figure 5c illustrates the HRTEM image of heterojunction constructed from Fe\(_2\)O\(_3\) and g-C3N4 based on this context.\[90\] The distinct interface of the two components can be clearly identified through the dark dotted line that are configured in the form of the Z-scheme (Figure 5d). Interesting phenomena occurs at the interface. Assisted by the internal static electric field, the photoinduced electrons in CB of \(\alpha\)-Fe\(_2\)O\(_3\) flow down and combine with the holes in valence band (VB) of g-C3N4. This allows more electrons for photocatalysis which can be corroborated from a 2.2 time higher rate of \(\text{CO}\) evolution for \(\alpha\)-Fe\(_2\)O\(_3–g\)-C\(_3\)N\(_4\) heterostructure than that produced by g-C3N\(_4\) alone (Figure 5e).

From various reports\[91\] about the electronic structure of graphene oxide, it can be envisioned that the bandgap of GO is still too large for visible light response. Meanwhile, Cu-based catalysts are known for effectively electrocatalytic reduction of \(\text{CO}_2\) to liquid products.\[92\] Controllable dispersion of Cu nanoparticles on the surface of GO can sum up the advantageous features of Cu and GO as can be exemplified from the work of Chen and co-workers.\[93\] Through a one-pot microwave method that involves mixing of GO with metal precursor, they found a \(\approx\)4–5 nm size of Cu NPs distributed on the GO surface (Figure 5f). The redox level of GO is found to be tunable with extent of Cu decoration (Figure 5g) in Cu–GO hybrid enabling highly selective generation of hydrocarbons from \(\text{CO}_2\). At the interface of the heterostructure, electrons transfer from GO to Cu nanoparticles favors charge separation and suppresses charge recombination. Thus, a 60 time higher rate of \(\text{CO}_2\) reduction was exhibited in the heterostructure as compared to the pristine component (Figure 5h). A step forward from metal nanoparticles, the current paradigm about metal-2D combination deals with single metal atom implantation on the 2D framework. The isolated metal atoms act as efficient active sites for \(\text{CO}_2\) reduction as well as the 2D network that immobilizes the active site and assists the charge transport kinetics.\[94–96\] Graphene derivative materials are ideal scaffolds for hosting single metal atoms. Their negatively charged surface contributes in uniformly anchoring the positive single-atom cations with maximal density. As compared to their nanoparticle counterparts,
isolated atoms have high activity and selectivity as has recently been exhibited from single Co atom[96] and single Ni atom in graphene[20,95] for electrocatalytic CO₂ reduction. Figure 6a shows HAADF-STEM image illustrating Co single atom dispersed with random distribution (yellow circles) on graphene. It has been observed that the metal–graphene contact is not a mere of physical adsorption rather there exists a chemical bond between isolated cobalt atom and the carbon through residual oxygen moieties on the surface of graphene (inset of Figure 6d). This special configuration renders the expected performance enhancement in photocatalytic CO evolution as compared to physically attached Co–graphene hybrid or pure graphene (Figure 6d). Unlike the metal nanoparticles dispersion, isolated single atoms guarantees a well-defined active site for studying the mechanism. For instance, Liu and co-workers[20] have recently employed operando X-ray absorption and photoelectron spectroscopy measurements to identify monovalent nickel (Ni⁺) single-atom center with d⁹ electronic configuration as catalytic active sites. This observation was made in a synthesized material of isolated single Ni atom anchored in N-doped graphene. The bright spots in Figure 6b of HAADF-STEM image represent the mentioned Ni-single atom without any cluster of nanoparticles. There exists a spontaneous charge transfer from monovalent Ni atom to the carbon atom of CO₂, which eases the reduction process. As shown in Figure 6e, the excellent performance for electrochemical production of CO gas can be realized from the specific current density of 350 A g⁻¹ cat⁻¹ at the overpotential of 0.6 V. The work by Jiang et al.[95] is another indicative for active single Ni atom anchored in graphene.
network. They prevented direct contact between water and the catalyst to suppress the competing hydrogen evolution reaction by using anion membrane electrode assembly as shown in Figure 6c. It is evident from Figure 6f that the selectivity toward CO production goes to $\approx 97\%$ while that of H$_2$ evolution is only 4%; and the accumulated CO production reaches $>630\, \text{mL}$ within 8 h of the electrocatalytic reaction. Given the fact that the 2D materials are ideal platforms to uniformly and densely disperse isolated single metal atoms, several beneficial properties can be envisioned from such interface in terms of mechanistic study and performance enhancement efforts.

Nevertheless, the overpotentials for CO$_2$ reduction reaction based on 2D heterostructured electrocatalysts remain substantially larger than the thermodynamic ones. This is due to the linear scaling of the binding energy of the intermediate products.\cite{97} Much more theoretical and experimental strategies should be developed to further improve the thermodynamic initiation and kinetics.

4. Conclusions and Perspectives

Heterostructures confer appealing etiquettes for catalysis as "a combined-two is better than an isolated-two." A plethora of advantageous features come to appear when the heterostructures are built from 2D materials. For instance, the electronic and structural variations endow a great opportunity in tuning the carrier distribution and mobility for enhanced activity. Moreover, some sorts of defects and dislocations derived from heterostructure formation are also appreciable for catalysis. The interface between two components will provide an opportunity to construct a microreactor. The recent progress on design and development of 2D based heterostructures will expectedly boost more research interests and efforts. Intriguing 2D materials such as graphene, g-C$_3$N$_4$, and MoS$_2$ have been frequently employed to design a novel heterostructure with various junction type and interesting results have been communicated. Another choice, i.e., transition metal phosphorus trichalcogenides with magnetic property, can be considered in the future. This will further widen the horizon of the arena with promising features for versatile catalytic applications.

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Conflict of Interest

The authors declare no conflict of interest.
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