

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-workers^[2] 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 available 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.^[4] The successful preparation of various 2D crystals^[11] 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.

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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.^[14] 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 ($2630 \text{ m}^2 \text{ g}^{-1}$)^[15] of graphene is also another feature. This can be associated with the increase of surface active sites which is quite beneficial for catalysis.^[16] The case of CO_2 reduction takes particular advantages from the graphene's large 2D π -conjugated structure, well consistent with the π -conjugated bond in CO_2 molecular. The initiation of a π - π conjugation interaction between graphene and CO_2 remarkably contributes to the adsorption of CO_2 molecules on the surface of graphene containing catalysts and eventually easing their reduction.^[17] Another intriguing feature that currently won the attention is the possibility of atomic dispersion in the graphene matrix.^[18–20] 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.^[21] Thus, various metal atoms, e.g., Ni,^[22] Co,^[23] 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 CO_2 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 $\text{g-C}_3\text{N}_4$ 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).^[24] In the case of $\text{g-C}_3\text{N}_4$, 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.^[25] 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 $\text{g-C}_3\text{N}_4$ than that in graphite (0.335 nm).^[26] The most intriguing feature of $\text{g-C}_3\text{N}_4$ 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, $\text{g-C}_3\text{N}_4$ possesses an appealing electronic structure with suitable bandgap for harvesting solar energy in a wider spectrum.^[26,27] The history of 2D $\text{g-C}_3\text{N}_4$ 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.^[27] This material is significantly robust and nonvolatile because its oxidation and reduction



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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

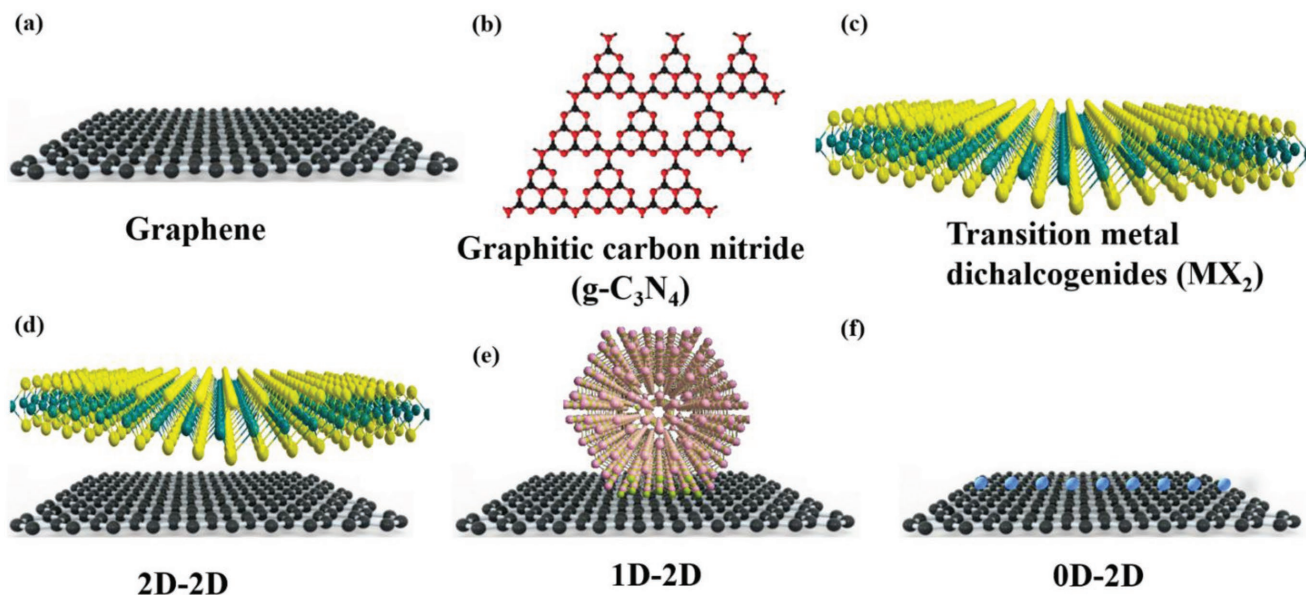


Figure 1. Frontiers of 2D materials used in catalysis and their heterostructures: a) graphene, b) g-C₃N₄, c) transition metal dichalcogenides, d) 2D-2D, e) 1D-2D, and f) 0D-2D.

is predictable that combining g-C₃N₄ with other 2D materials, e.g., MoS₂,^[28] NiFe-LDH,^[29] 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.^[30,31] 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.^[31] 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.^[31] Moreover, the 2D TMD nanosheets could be achieved by exfoliation of bulk crystals or building up individual atoms via vapor deposition.^[32] 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^[33] 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.^[34] 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. Heterostructuring 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),^[35] layered double hydroxides,^[36] metal-organic frameworks (MOFs),^[37] 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.^[38] Some of them are explored for catalyzing water splitting. For example, Mo₂CT_x was theoretically and experimentally studied by She et al.^[39] 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 Mo₂CT_x are catalytically active toward HER, which is different with the case in hexagonal phased MoS₂.

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

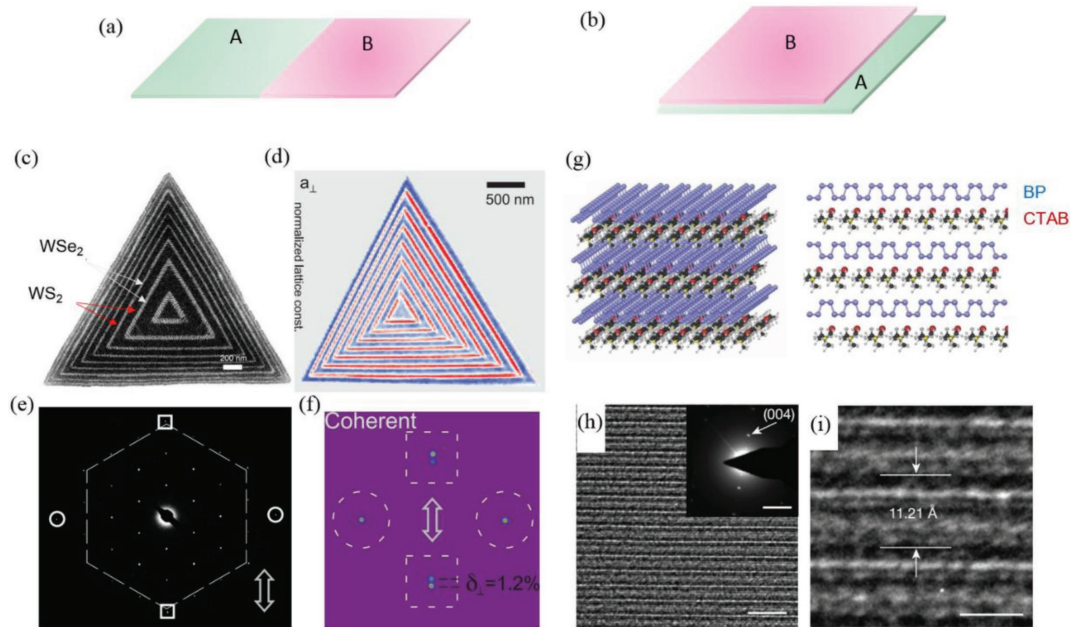


Figure 2. a,b) Schematic illustration of typical architectures of lateral (a) and vertical (b) heterostructures based on 2D materials. c) Scanning electron microscopy (SEM) image of monolayer WS_2/WSe_2 superlattice. d) Spatial maps of normalized lattice constants a_{\perp} . e) SEAD pattern of superlattice. f) Enlarged diffraction spots as indicated in (e). g) 3D and cross-sectional views of the simulated atomic structure of the P/CTAB lattice. h,i) Cross-sectional TEM images in different resolution. c–f) Reproduced with permission.^[49] Copyright 2018, American Association for the Advancement of Science. g–i) reproduced with permission.^[57] Copyright 2018, Macmillan Publishers Limited, part of Springer Nature.

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.”^[6,41] 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_{\perp} (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

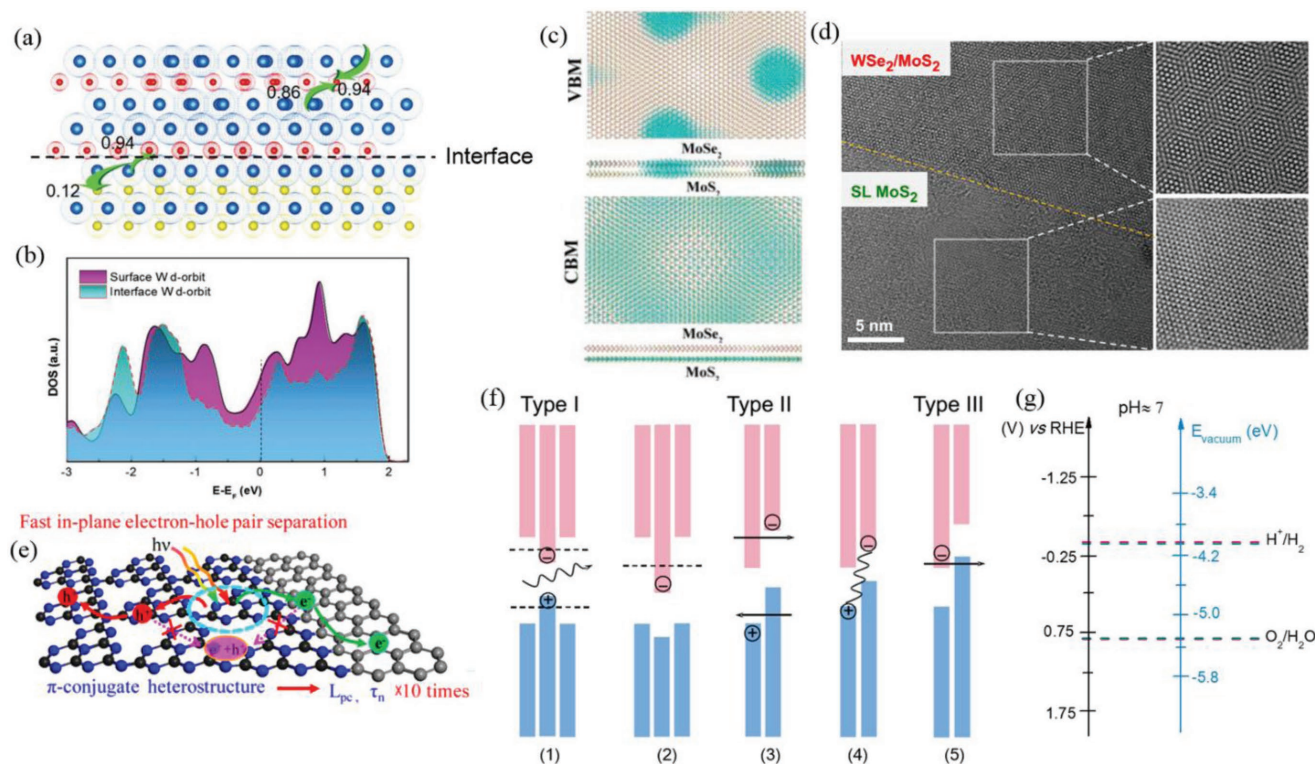


Figure 3. a) Charge redistribution in $WS_2@WS_2$ heterostructure. b) The density of states comparison of the W atom on the surface and interface around the Fermi level. a,b) Reproduced with permission.^[61] Copyright 2017, Wiley-VCH. c) Top view and side view of the spatial distribution of VBM and CBM states for the Moire structure. Reproduced with permission.^[65] Copyright 2013, American Chemical Society. d) High-resolution TEM images of a boundary region of single-layer MoS_2 and the hetero-bilayer, showing the resulting Moire pattern. Reproduced with permission.^[59] Copyright 2014, National Academy of Sciences. e) Schematics depicting photocarrier transfer between $C_{ring}-C_3N_4$. L_{pc} and τ_n represent the photocarrier diffusion length and lifetime, respectively. Reproduced with permission.^[67] Copyright 2017, American Chemical Society. f) Illustration of type I, II, and III heterostructures and their applications, where red and blue indicate conduction and valence bands, respectively. Reproduced with permission.^[69] Copyright 2016, American Physical Society. g) Redox potentials of water at $pH \approx 7$.

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 a_{\parallel} (parallel to the heterointerfaces) orientation confirm the perfect lattice matching. And similar lattice constants were also observed in the diffraction data corresponding to a_{\perp} (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^[50] (i.e., Bi_2Se_3 , In_2Se_3), semiconductors^[51] (i.e., MoS_2 ^[52]) and metals (i.e., MoC_2 ^[53]). In the past few years, a variety of TMD heterostructures have been prepared via epitaxial growth method^[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 provide 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_2C with WS_2 , an apparent electron of 0.12 $|e|$ transfer from the W atoms of W_2C 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 (ΔG_{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 $\text{MoSe}_2/\text{MoS}_2$ 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 $\text{WSe}_2/\text{MoS}_2$ heterostructure^[59] 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 $\text{C}_{\text{ring}}\text{-C}_3\text{N}_4$ plane heterostructural nanosheet,^[67] 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^[68] 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.^[69] 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),^[70] photocatalysis ((3) and (4))^[7] or electronic devices (2).^[71] 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 CO_2 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.^[72] 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 wide-spread 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^[73] 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 MoS_2 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 MoS_2 and reduced graphene oxide.^[62] MoS_2 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 MoS_2 -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 (MoS_2 nanoparticles or rGO). It has, recently, been observed that graphene-mediated charge-transfer kinetics can result in synergizing the 2D–2D heterostructure between Mo_2C and graphene.^[74] With the optimized reaction time and CH_4 flow rate in chemical vapor deposition (CVD) operation, the controllable nucleation of Mo_2C flakes on graphene sheet has been observed as depicted in Figure 4a. In due course of the reaction, Mo_2C flakes first nucleate on already formed graphene sheet. As the reaction time increases, further nucleation of Mo_2C 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 Mo_2C flakes and the excellent electronic coupling to graphene, collectively contributing to rapid charge transfer kinetics for H^+ adsorption and H_2 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 ₂ -hydrogenated graphene	2D–2D	Solvothermal	Ultrathin MoS ₂ nanosheets grown on hydrogenated graphene	structural and electronic modulations	HER	$\eta_{10} = 124$ mV, Tafel slope = 41 mV decade ⁻¹ , TOF _{200mV} = 7.8 s ⁻¹	[98]
MoS ₂ -graphene	0D–2D	Hydrothermal reaction of (NH ₄) ₂ MoS ₄ with hydrazine in DMF solution containing mesoporous graphene foam as the matrix	Well-dispersed and ultrathin MoS ₂ nanoparticles (~2 nm) were grown on the graphene	<ul style="list-style-type: none"> Abundance of catalytic edge sites, The increase in electrochemically accessible surface area The unique synergic effects between the graphene and MoS₂ 	HER	$\eta_{100} = 200$ mV, onset = 100 mV, Tafel slope = 42 mV decade ⁻¹	[99]
MoS ₂ -rGO	2D–2D	Intercalation via solvent evaporation	Layer confined structure of MoS ₂ -rGO	oxidation degree of graphene, the crystallinity of MoS ₂ , and the exposed active site affect the catalytic activity	HER	$\eta_{23} = 200$ mV, onset = 140 mV, Tafel slope = 41 mV decade ⁻¹	[100]
MoS ₂ -rGO	0D–2D	Solvothermal synthesis of MoS ₂ nanoparticles on rGO sheets suspended in solution	Few-layer and nonaggregated MoS ₂ structures with an abundance of exposed edges stacked onto graphene sheet	strong chemical and electronic coupling between the GO sheets and MoS ₂	HER	onset = 100 mV, Tafel slope = 41 mV decade ⁻¹	[62]
MoS ₂ -rGO	2D–2D	Sonication, followed by solvothermal	MoS ₂ nanosheets grown on the rGO sheets	confined growth of MoS ₂ on the GO sheets results in rich active edges and improved electrical conductivity	HER	onset = 0.13 V, $\eta_{10} = 218$ mV, Tafel slope = 57 mV decade ⁻¹	[101]
MoS ₂ -N doped graphene	2D–2D	Vacuum-assisted filtration followed by electrodeposition	Amorphous MoS ₂ matrix electrodeposited on graphene to give hydrated 3D framework	The hydrogel framework in the composite structure enhances the electrode wettability and facilitate the access to electrolytes	HER	$\eta_{10} = 140.6$ mV, Tafel slope = 105 mV decade ⁻¹	[102]
Cu–MoS ₂ -rGO	2D–2D	Sonication followed by solvothermal	MoS ₂ nanoflowers with crumpled nanosheets dispersed on 2D graphene	<ul style="list-style-type: none"> Plenty of folded edges exposed rGO improved the electrical conductivity of the catalyst 	HER	onset = 126 mV, $\eta_{83.6} = 400$ mV, Tafel slope = 90 mV decade ⁻¹	[103]
rGO–WS ₂	2D–2D	Hydrothermal, CVD, sensitization	rGO nanosheets dispersed on the surface of vertically oriented WS ₂ nanosheets	synergism from the decoration by rGO through a remarkable area of contact on WS ₂ surface that enhanced the electron transport phenomena	HER	$\eta_{10} = 229$ mV, Tafel slope = 73 mV decade ⁻¹	[63]
MoS 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 ₂ nanosheets to the electrode	HER	onset = 0.09 V, Tafel slope = 44.6 mV decade ⁻¹ , TOF _{0mV} = 0.06 s ⁻¹	[104]
MoS ₂ -N-doped CNT	2D–1D	Plasma-enhanced chemical vapor deposition followed by thiomolybdate decomposition	Amorphous molybdenum sulfide (MoS 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, $\eta_{10} = 110$ mV, Tafel slope = 40 mV decade ⁻¹ , TOF _{200mV} = 3.5 s ⁻¹	[105]
MoS ₂ -C nanosheet	2D–2D	Microemulsion procedure	Defect rich hierarchical spheres in which MoS ₂ nanosheets grew outwards from the inner core	The S ions produced from CS 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, $\eta_{10} = 159$ mV, Tafel slope = 56.1 mV decade ⁻¹	[106]

Table 1. Continued.

Heterostructures	Type of junction	Synthesis methods	Structural features	Unique properties	Applications	Performance	Ref.
Mo ₂ C-graphene	2D-2D	Catalyst-assisted CVD	Centimeter range Mo ₂ C hexagonal film grown on in situ formed graphene	Enhanced charge transfer kinetic across the interface	HER	onset = 87 mV, η_{10} = 236 mV, Tafel slope = 73 mV decade ⁻¹	[74]
MoO ₂ -MoS ₂	0D-2D	Hydrothermal method followed by sulfurization by H ₂ S	MoS ₂ sheets contour the surface of most of the MoO ₂ crystals	MoO ₂ surface can sulfide by inward progression of MoO ₂ (20-2)/MoS ₂ (002) interfaces resulting in upright-oriented and edge exposing MoS ₂ sheets	—	—	[107]
MoO ₂ -MoSe ₂	2D core-shell	CVD method followed by calcination under Se atmosphere	Trapezoid-like MoO ₂ /MoSe ₂ core-shell nanosheets grown on the substrate	High crystalline mismatch between MoO ₂ and MoSe ₂ provides defects and dislocations	HER	onset = 63 mV, η_{10} = 181 mV, Tafel slope = 49.1 mV decade ⁻¹	[108]
ZnIn ₂ S ₄ -MoS ₂ -rGO	0D-2D	Hydrothermal	ZnIn ₂ S ₄ nanoparticles uniformly dispersed on MoS ₂ -rGO nanosheet without aggregation	Creation of abundant active sites with improved charge separation	HER	H ₂ evolution rate = 425.1 $\mu\text{mol h}^{-1} \text{g}^{-1}$	[109]
ZnIn ₂ S ₄ -g-C ₃ N ₄	2D-2D	Thermal polymerization, exfoliation, hydrothermal	"sheet-on sheet"-like structure wherein layered surfaces of g-C ₃ N ₄ nanosheet are covered with ZnIn ₂ S ₄ nanosheets	Efficient interfacial transfer of photoinduced electrons and holes from g-C ₃ N ₄ to ZnIn ₂ S ₄ nanosheets	Photo. HER	H ₂ evolution rate = 14.1 $\mu\text{mol h}^{-1}$	[110]
Co,N-codoped CNT-graphene	2D-1D	Pyrolysis followed by acid etching of the precursors (g-C ₃ N ₄ and Co source)	a CNT/graphene-like heterostructure encapsulated with Co NPs - Co NPs are covered by a 10-20 layered graphitic wall	Excellent catalysis due to synergic effects of the heterostructure containing different catalytically active sites	ORR and HER	ORR: onset = 0.96 V, half-wave potential = 0.85 V, Tafel slope = 65 mV decade ⁻¹ , HER: onset = 59 mV, η_{10} = 123 mV, Tafel slope = 67 mV decade ⁻¹	[111]
Co ₃ O ₄ @C-N nanosheet arrays	0D-2D	Electrodeposition, CVD	Co ₃ O ₄ NPs uniformly anchored on sp ² -hybridized carbon-nitrogen nanosheet array	The Co ₃ O ₄ NPs uniformly anchored on the nanosheet array brings about more active sites, boosting mass transport and electron transfer	OER	η_{25} = 245 mV, Tafel slope = 65 mV decade ⁻¹ , TOF _{370mV} = 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	onset = 1.48 V, η_{10} = 300 mV, Tafel slope = 123 mV decade ⁻¹ , TOF _{370mV} = 1.4 s ⁻¹	[113]
NiPS ₃ nanosheet-graphene	2D-2D	Sonication	The small NiPS ₃ nanosheets uniformly attached on the basal planes of large graphene sheets	The greatly increased active surface area and significantly decreased electron transfer resistance caused by the synergistic effect	OER	onset = 1.48 V, η_{10} = 294 mV, Tafel slope = 42.6 mV decade ⁻¹ , TOF _{370mV} = 0.0249 s ⁻¹	[114]
FeNi-LDH/Ti ₃ C ₂ -MXene	2D-2D	Centrifugation, freeze-drying	Ionic heteroassembly of interconnected porous network of FeNi-LDH nanoplates on Ti ₃ C ₂ MXene nanosheets	Prominent charge transfer from LDH to MXene is identified to accelerate the redox process	OER	onset = 1.47 V, η_{10} = 298 mV, Tafel slope = 43 mV decade ⁻¹ , TOF _{300mV} = 0.26 s ⁻¹	[115]

Table 1. Continued.

Heterostructures	Type of junction	Synthesis methods	Structural features	Unique properties	Applications	Performance	Ref.
CdS–MoS ₂	1D–2D	Glucose-assisted hydrothermal	MoS ₂ nanosheets oriented vertically on CdS nanowire	High exposure of the active edge sites and increased charge separation and transfer rate	Photo. HER	H ₂ evolution rate = 9.73 mmol h ⁻¹ g ⁻¹ apparent quantum efficiency _{4,20nm} = 60.3%	[116]
MoS ₂ -graphene–TiO ₂	0D–2D–2D	Hydrothermal	– TiO ₂ nanoparticles grown on layered MoS ₂ -graphene hybrid sheet – MoS ₂ nanosheets dispersed on graphene sheets	MoS ₂ nanosheets on graphene sheets accept electrons from the CB of TiO ₂ and facilitate hydrogen production	Photo. HER	H ₂ evolution rate = 165.3 μmol h ⁻¹ apparent quantum efficiency _{365nm} = 9.7%	[81]
MoS ₂ -rGO	2D–3D	CVD and Hammer's method	Heterojunctions composed of 3D nanoporous reduced graphene oxide as visible light absorber and 2D monolayer MoS ₂ 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 MoS ₂ for increased HER	Photo. HER	onset = 48 mV, η ₁₀ = 141 mV, Tafel slope = 61 mV decade ⁻¹	[117]
MoS ₂ -g-C ₃ N ₄	0D–2D	Hydrothermal	MoS ₂ quantum dots dispersed uniformly on the surface of g-C ₃ N ₄	The heterojunction promotes the separation of photoinduced charge carriers and enhance water splitting reaction	Photo. HER	H ₂ evolution rate = 1.42 mmol h ⁻¹ g ⁻¹	[118]
MoS ₂ /WS ₂ WS ₂ /MoS ₂	2D–2D	A two-step CVD method	Well-defined triangular sheets of WS ₂ (or MoS ₂) are uniformly deposited on monolayer MoS ₂ /Au (or WS ₂ /Au)	Effective electron–hole separation and fast electron transfer kinetics assisted by Type-II band alignment	Photo. HER	H ₂ evolution rate = 1.819 μmol h ⁻¹ cm ⁻²	[54]
MoS ₂ /g-C ₃ N ₄ /GO	0D–0D–2D	Hummers' method, sonication, condensation polymerization	Quantum dots of C ₃ N ₄ and MoS ₂ are dispersed with slight aggregation on the surface of graphene oxide sheet	Energy bands are aligned such that the collection of electrons are in MoS ₂ and holes are in g-C ₃ N ₄	Photo. HER	H ₂ evolution rate = 1.65 mmol h ⁻¹ g ⁻¹	[82]
Zn _{1-x} Cd _x S-rGO (x = 0.8)	0D–2D	Coprecipitation–hydrothermal	Nanoparticles of Zn _x Cd _{1-x} S dispersed on the surface of rGO sheet	– rGO serves as electron collector and transporter – the photoinduced electrons in CB of Zn _{0.8} Cd _{0.2} S tend to transfer to rGO, leading to enhanced charge carrier separation	Photo. HER	H ₂ evolution rate = 1824 μmol h ⁻¹ g ⁻¹ apparent quantum efficiency _{4,20nm} = 23.4%	[119]
g-C ₃ N ₄ -MoS ₂	2D–2D	Impregnation of mesoporous carbon nitride with an aqueous solution of (NH ₄) ₂ MoS ₄ , followed by sulfuration	Slabs of MoS ₂ deposited on the surface of mesoporous carbon nitride sheet and form a thin junction	The intimate thin junction ensured short carrier transport distance owing to the electron-tunneling effect through MoS ₂ thin layers to reaction interfaces	Photo. HER	H ₂ evolution rate = 20.6 μmol h ⁻¹	[28]
CdS–WS ₂ -g-C ₃ N ₄	2D–2D	Hydrothermal, exfoliation, chemical impregnation method	WS ₂ 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	H ₂ evolution rate = 1174.5 μmol h ⁻¹ g ⁻¹	[120]
Phosphorene-g-C ₃ N ₄	2D–2D	Self-assembly via physical mixing	The g-C ₃ N ₄ nanosheets are deposited on the surface of phosphorene nanosheet	Intimate electronic coupling between the components contributes to enhanced charge separation	Photo. HER	H ₂ evolution rate = 571 μmol h ⁻¹ g ⁻¹ apparent quantum efficiency _{4,20nm} = 1.2%	[121]

Table 1. Continued.

Heterostructures	Type of junction	Synthesis methods	Structural features	Unique properties	Applications	Performance	Ref.
g-C ₃ N ₄ -C _{ring}	Lateral 2D-2D	Hydrothermal conjugation	Sheet-like (C _{ring})-C ₃ N ₄ homogeneously connected without the growth of nanoparticles.	Improved charge carrier separation and fast spatial transport of photoinduced electrons assisted by in-plane π -conjugated electric field	Photo. water splitting	H ₂ evolution rate = 371 $\mu\text{mol h}^{-1} \text{g}^{-1}$ apparent quantum efficiency _{420nm} = 5%	[67]
g-C ₃ N ₄ -NiAl-LDH	2D-2D	Thermal condensation, exfoliation, hydrothermal	Ultrathin 2D LDH sheets grown on g-C ₃ N ₄	Electrostatic self-assembly between positively charged NiAl-LDH sheets and negatively charged g-C ₃ N ₄ nanosheets form an intimate interface promoting fast electron transfer	Photo-CO ₂ red.	CO evolution rate = 8.2 $\mu\text{mol h}^{-1} \text{g}^{-1}$	[122]
rGO-CdS	2D-1D	Microwave-assisted hydrothermal	CdS nanorods dispersed on rGO sheets	<ul style="list-style-type: none"> The 1D CdS nanorod act as electron acceptor and transporter; The rGO facilitates the CO₂ adsorption and activation 	Photo-CO ₂ red.	CH ₄ evolution rate = 2.51 $\mu\text{mol h}^{-1} \text{g}^{-1}$ apparent quantum efficiency _{420nm} = 0.8%	[87]
Cu-graphene oxide	0D-2D	Microwave heating	Cu nanoparticles dispersed on the surface of few layered graphene oxide sheet	<ul style="list-style-type: none"> 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 $\mu\text{mol g}^{-1} \text{h}^{-1}$	[93]
TiO ₂ -graphene-MoS ₂	2D-2D	Hammers method, hydrothermal method	2D rGO sheets assembled into macroporous 3D structures on which TiO ₂ nanoparticles and MoS ₂ nanosheets are uniformly distributed	The electrons 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 $\mu\text{mol g}^{-1} \text{h}^{-1}$	[123]
g-C ₃ N ₄ -CO	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 $\mu\text{mol g}^{-1}$	[88]
g-C ₃ N ₄ -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 $\mu\text{mol g}^{-1} \text{h}^{-1}$ apparent quantum efficiency _{420nm} = 0.963%	[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 (!) Ni atomic center having d ⁹ electronic configuration act as active site to reduce CO ₂	Electrocatal CO ₂ red.	Faradaic efficiency = 97% TOF _{0.61 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	Electrocatal CO ₂ red.	CO selectivity _{550 mV} = 95% TOF _{0.57 V} = 6.8 s ⁻¹	[95]

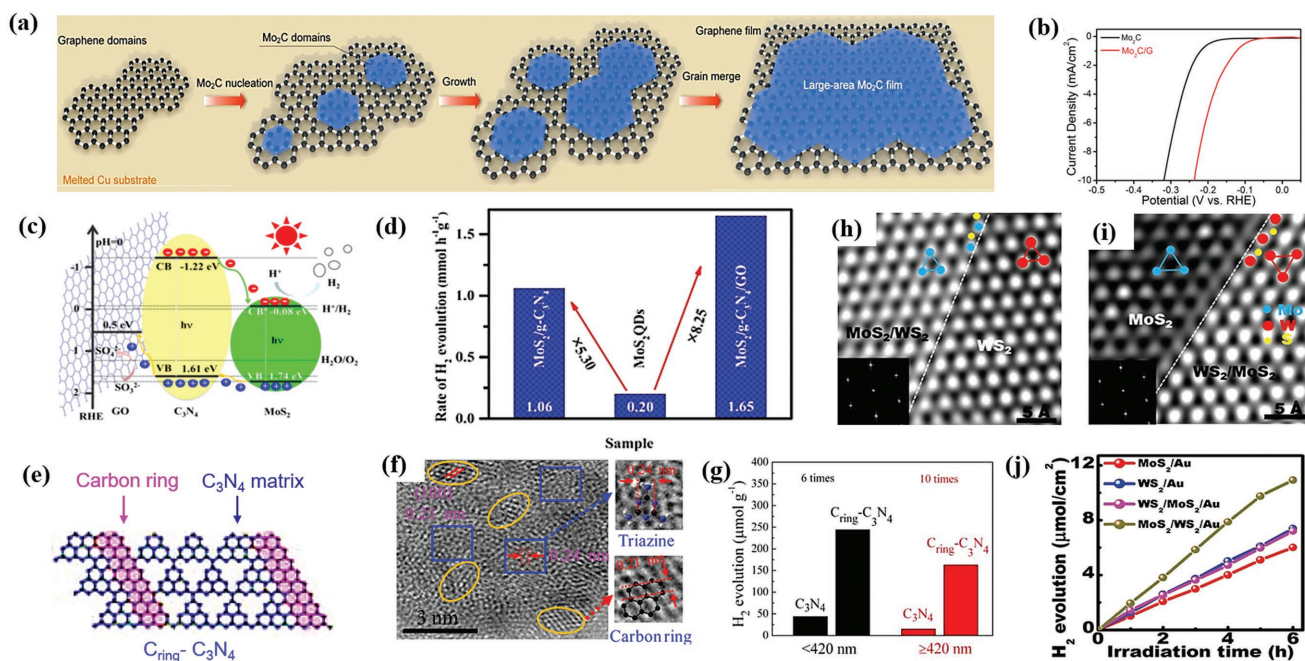


Figure 4. a) Schematics illustrating the growth of Mo₂C crystals on graphene exemplifying 2D–2D heterostructure. b) Polarization curves for HER catalytic activities of Mo₂C and Mo₂C/graphene. a,b) Reproduced with permission.^[74] Copyright 2017, Wiley-VCH. c) Schematics of charge carrier separation across the MoS₂/g-C₃N₄/GO interface. d) Photocatalytic HER performance depicting remarkable enhancement for the heterojunction. c,d) Reproduced with permission.^[82] Copyright 2017, American Chemical Society. e) Schematic depicting the lateral C_{ring}/C₃N₄ heterostructure and f) the corresponding HRTEM image. g) Photocatalytic H₂ evolution under UV (<420 nm) and visible light (≥420 nm) per hour. e–g) Reproduced with permission.^[67] Copyright 2017, American Chemical Society. h) Atomic-resolution STEM-HAADF image from the edge of WS₂/MoS₂ stack. i) Atomic-resolution STEM-HAADF image from the edge of MoS₂/WS₂ stack. j) Photocatalytic H₂ evolution curves of heterostructures in (h) and (i) under solar light irradiation. h–j) Reproduced with permission.^[54] Copyright 2016, Wiley-VCH.

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.^[75] 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^[76] fabricated the in-plane black phosphorus/Co₂P heterostructure for electrocatalytic water splitting in alkaline media (1.0 M KOH). The high oxygen evolution activity is also realized using BP/Co₂P heterostructure. Besides, the vertical 2D heterostructures, such as Ni₃FeN/NRGO,^[77] were designed for improving OER performance. The strong coupling between Ni₃FeN 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.^[78]

It obvious that plethora of reports^[79] have been made in attempt to boost the photocatalytic performance of TiO₂ since its first observation by Fujishima and Honda.^[80] The synergetic effect between MoS₂ and graphene in cocatalyzing HER on the surface of TiO₂ can be considered as one of the efforts.^[81] This heterostructure has two prominent advantages: i) graphene has high electron mobility, and hence the electrons on the conduction band (CB) of TiO₂ can be injected to the graphene sheet and experience accelerated kinetics; ii) the MoS₂ 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 MoS₂ quantum dots (QDs), g-C₃N₄ 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 MoS₂ and holes in g-C₃N₄.^[82] This configuration ensures charge separation and effectively suppress recombination (Figure 4c). The MoS₂ QDs are closely spaced with those of g-C₃N₄ which is intimately contacted with graphene, depicting the junctions of MoS₂ to g-C₃N₄ 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-C₃N₄ have lone pair of electrons which would confer an ideal platform for an intimate connection of components in heterostructures.^[83] 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 π -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 sp²-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_{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 MoS₂ and WS₂ (as MoS₂/WS₂ or WS₂/MoS₂ 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 WS₂/MoS₂ and MoS₂/WS₂, 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 MoS₂/WS₂ 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. CO₂ Reduction

The reduction of CO₂ involves the breaking of the C=O bond and the formation of products such as carbon monoxide (CO), formate (CHOO), formaldehyde (HCHO), methanol (CH₃OH), methane (CH₄), ethanol (C₂H₄OH), etc. Unlike HER, the reduction of CO₂ 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 CO₂ 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 CO₂ reduction; they maximize specific surface area and contribute to proliferation of active sites. Moreover, the interaction between graphene and CO₂ takes a special advantage. There is also a delocalized π - π conjugation system

in CO₂ molecule. This π - π conjugation interaction between CO₂ and graphene could ease CO₂ adsorption and activation.^[86,87] Ong et al.^[88] have experimentally demonstrated this interaction using a 2D–2D hybrid structure obtained via π - π 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 CH₄ (product of CO₂ 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 Fe₂O₃ 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 α -Fe₂O₃ flow down and combine with the holes in valence band (VB) of g-C₃N₄. This avails more electrons for photocatalysis which can be corroborated from a 2.2 time higher rate of CO evolution for α -Fe₂O₃-g-C₃N₄ heterostructure than that produced by g-C₃N₄ 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 CO₂ 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 CO₂. 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 CO₂ 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 CO₂ reduction as well as the 2D network that immobilizes the active site and assists the charge transfer kinetics.^[20,94–96] 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,

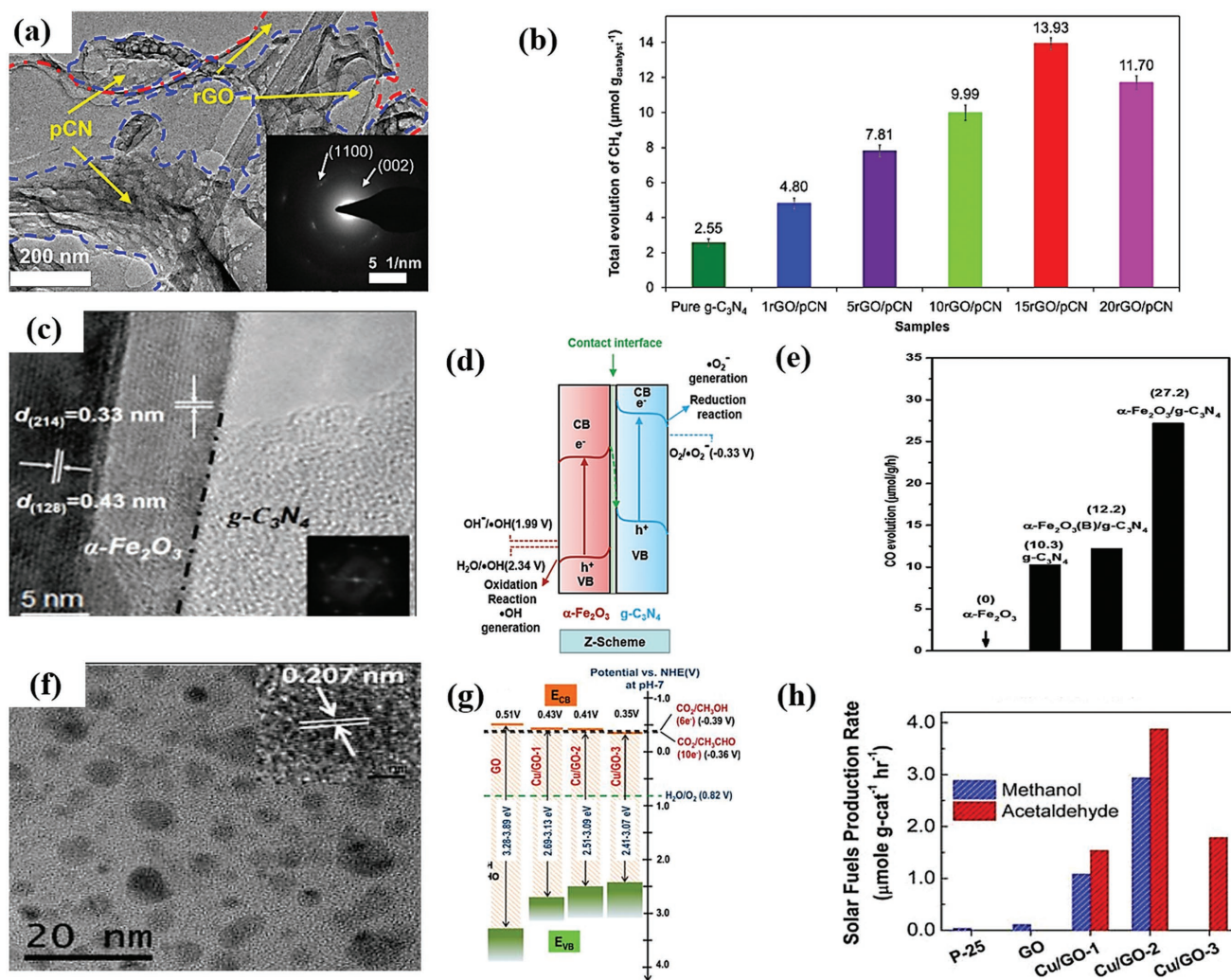


Figure 5. a) TEM image of protonated graphitic carbon nitride–reduced graphene oxide (rGO–pCN) composite materials. b) Photocatalytic CH₄ production rate using various samples evidencing the optimized composite with the highest rate. a,b) Reproduced with permission.^[88] Copyright 2015, Elsevier Ltd. c) HRTEM image of Fe₂O₃–g-C₃N₄ composite with distinct interface. d) Schematic showing the Z-scheme type heterostructure between Fe₂O₃ and g-C₃N₄. e) Photocatalytic CO production rate as a CO₂ reduction product using evidencing the heterostructure with the highest rate. c–e) Reproduced with permission.^[90] Copyright 2018, Wiley-VCH. f) TEM (inset HRTEM) image of Cu–GO heterostructure. g) Band edge positions for various Cu–GO ratios relative to CO₂/CH₃OH and CO₂/CH₃CHO formation potentials. h) Photocatalytic CO₂ reduction performance (fuel production rate) different ratio of Cu–GO depicting that Cu/GO-2 is the optimum one. f–h) Reproduced with permission.^[93] Copyright 2014, American Chemical Society.

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_{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

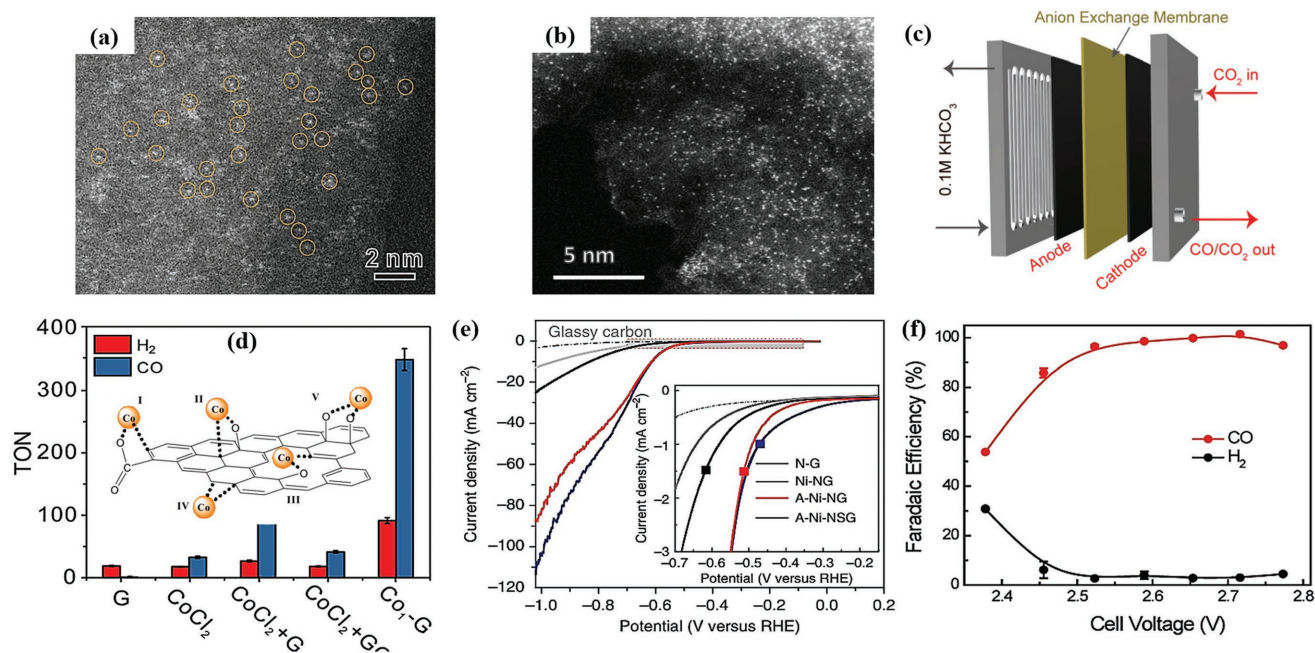


Figure 6. a,b) HAADF-STEM images for a single Co atom (yellow circle) dispersed in a graphene matrix (a) and a single Ni atom dispersed in nitrogen-doped graphene (b). c) Setup of anion membrane electrode assembly for suppressing HER. d) Electrocatalytic CO₂ reduction performance depicted in terms of turnover number (TONs) of CO and H₂ production by Co (single atom)-graphene nanosheets (inset: schematics of showing the bonding of Co with graphene framework). e) Linear sweep voltammograms obtained in CO₂-saturated 0.5 M KHCO₃ solution for CO₂ reduction performance (N-G, nitrogenated graphene; Ni-NG, metallic Ni-nanoparticle-decorated nitrogen-doped graphene; without sulfur precursor (A-Ni-NG), with sulfur precursor (A-Ni-NSG)). f) Faradaic efficiency of H₂ and CO production from the setup in (c) evidencing high selectivity for CO production on the surface of single-atom-graphene heterostructure. a,b) Reproduced with permission.^[18] Copyright 2018, Wiley-VCH. c,f) Reproduced with permission.^[95] Copyright 2018, The Royal Society of Chemistry. d,e) Reproduced with permission.^[20] Copyright 2018, Macmillan Publishers Limited, part of Springer Nature.

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 ≈97% while that of H₂ evolution is only 4%; and the accumulated CO production reaches >630 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 CO₂ 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.^[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-C₃N₄, and MoS₂ 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.

Keywords

2D materials, catalysis, heterostructures, synergism

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