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Group-VI-Chalcogenide-Based Nanomaterials in Photo/Thermal Organic Transformations

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Cite This: *Acc. Mater. Res.* 2022, 3, 1033−1048

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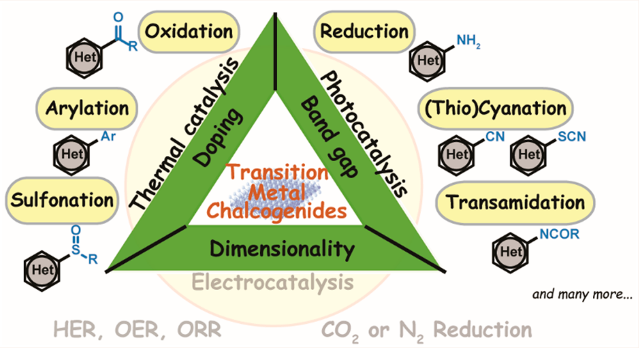


CONSPECTUS: With the growing awareness of the need to have greener, economical, and sustainable alternatives in synthetic chemistry, the scientific community has come up with strategies that are based on materials in general and nanomaterials in particular. Nanomaterials can be tuned to obtain the desired properties. These methods include modification of the surface by functionalization, controlling the defects at the edge and the basal plane, and doping with metals, other nanomaterials, or heteroatoms. At the lower dimensions, they bear an enhanced surface-to-volume ratio. These act as potential sites for catalysis, and hence, nanomaterials have an immense ability to mediate organic transformations. Although these have not yet taken over the reported metal/ligand-based catalysts completely, one can agree to the fact that nanoscience and nanotechnology have a charisma of their own. Over the years, they have acquired importance in industries as well, chiefly because of their heterogeneous nature that allows one to reuse them in subsequent runs. In this Account, we have made an effort to introduce the readers to the various forms of transition metal chalcogenides (TMCs) that have been used in photo or thermal catalysis as well as our contributions in this regard. To date, various accounts or reviews centered around these materials have focused chiefly on energy related applications or electrocatalytic transformations like the water-splitting process, the hydrogen evolution reaction (HER), and the oxygen evolution/reduction reaction (OER/ORR) and electronics such as transistors, solar cells, photodetectors, etc. Also, these materials have gained popularity in drug delivery systems and sensing applications. Very few reports have brought about the role of TMCs in catalysis. Herein, we have laid emphasis on the use of these materials in organic transformations, chiefly categorized as oxidation−reduction reactions and C−C or C−heteroatom bond forming reactions, mediated thermally or photochemically. It is also possible to merge the multifaceted applications of TMCs, as demonstrated in our recent report on the cross dehydrogenative coupling (CDC) reaction synchronized with HER. Apart from this, we have discussed some of the other reactions such as hydrodesulfurization (HDS) and hydrodeoxygenation (HDO) as well. Some of the key challenges persisting in this field include the design of chiral materials for various enantioselective or diastereoselective reactions, correlation of the experimental output with theoretical studies, controlling the extent of doping, and detailed analysis of TMCs mediated organic transformations. In a nutshell, TMC mediated catalysis is a relatively unexplored, yet a highly promising field, and overcoming these challenges would enhance the potential of this field manifold in various sectors.

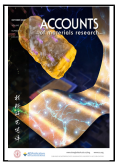
1. INTRODUCTION

Towards the later part of the 19th century, researchers were interested in determining the factors that could result in a significant change in the property/properties of various materials. One such factor was the dimensionality. The discovery of GR in 2004 marked the onset of the development of 2D nanomaterials that were found to possess certain remarkable properties compared to their bulk counterparts.[1] These could, however, be exploited only after modification of the native GR, for instance, by functionalization. This was a tremendous drawback for this material.

Soon after, researchers shifted their focus to a new class of materials commonly known as the TMDs. These are a family of layered materials that were first discovered by Linus Pauling in 1923.[2] Later, in 1986, Joensen and co-workers achieved the synthesis of 2D-MoS$_2$ using the chemical exfoliation method.[3] Apart from TMDs, MXenes[4] are among the other well-known layered materials. The chemistry of TMDs opened up new horizons in the fields of electronic and photovoltaic devices, energy storage, etc. (Figure 1).

TMDs represent a class of metal dichalcogenides of the formula MX$_2$, where M is a transition metal from group IV (Ti,

Received: June 20, 2022
Revised: August 16, 2022
Published: September 5, 2022



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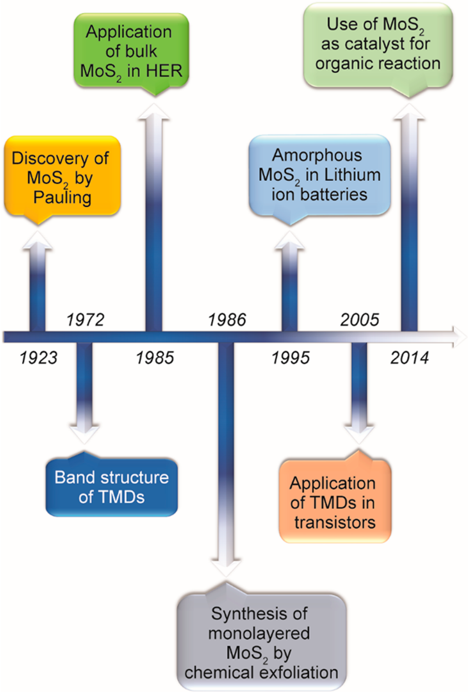


Figure 1. Developments in the field of TMD-based nanomaterials over the years.[10−14]

Zr, Hf), group V (V, Nb, Ta), or group VI (Mo, W) and X is a chalcogen (S, Se, Te). Each layer of transition metal (e.g., Mo, W, Nb) is sandwiched between two chalcogen layers by a weak van der Waals' force. Consequentially, bulk TMDs can be converted to single or few layers by electrochemical or chemical exfoliation by lithium-ion intercalation[5] and solvent assisted mechanical exfoliation.[6] Monolayered or few-layered TMDs exhibit a variety of properties that are not seen in bulk materials.[7] For example, bulk MoS_2 exists in a semiconducting 2H phase with an indirect bandgap of 1.23 eV, whereas monolayered MoS_2 has a direct bandgap of 1.84 eV.[8] Experimental and theoretical reports suggest that TMDs exist in various polymorphs, out of which 1T and 2H are the most common ones. The overall arrangement is hexagonal, with each M coordinated to six X. More specifically, the 2H phase is trigonal prismatic, and the 1T phase is octahedral.[9]

The coexistence of the two polymorphs is not uncommon, rather, they have shown superior activity in HER[15] and organic transformations.[16] This extraordinary property is attributed to the presence of metal−semiconductor heterojunctions. TMDs with both the polymorphs coexisting in the same basal plane are designated as the mixed phase type.[17] The exact structure and morphology post-preparation can be realized precisely by various forms of spectroscopy and microscopy.[8] For example, the presence of monolayered material is confirmed by atomic force microscopy (AFM). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) confirm the crystallinity of the material. One can extract a plethora of information from this data. This includes the *d*-spacing, diffraction angle, etc. Though scanning electron microscopy (SEM) allows one to obtain a picture of the layered flakes, X-ray photoelectron spectroscopy (XPS) confirms the elemental composition. UV−visible and Raman spectroscopy give us the signature peaks of TMDs, and the powder X-ray diffraction (PXRD) pattern can be used to demarcate a decrease in the number of stacked layers. All these are indicative of a successful breakdown of dimensionality from the bulk material (Figure 2).

The change in dimensionality results in the generation of a greater number of active sites in the 2D material as a consequence of the enhanced surface-to-volume ratio. Researchers became interested in exploring the potential of TMCs to mediate organic transformations as heterogeneous catalyst. This feature was particularly interesting, for it provided us the scope to replace organic catalysts by relatively cheaper, earth-abundant TMCs. Efforts were directed towards the design of a relatively easier synthetic strategy that could be eco-friendly, less time-consuming, and recyclable with the generation of minimal byproduct(s). Indeed, various groups reported that TMCs and their doped or composite analogues could mediate organic transformations thermally, photochemically, and electrochemically.[21]

The current account encompasses organic transformations mediated by TMCs or their composite analogues thermally or photochemically as well as our contributions in this regard. Various review papers on TMCs have mainly focused on particular applications (Figure 3) such as CO_2 reduction, energy storage, batteries, etc. Electrocatalysis is also a field that has grown tremendously with this class of nanomaterials and broadly encompasses hydrogen evolution reaction, the oxygen evolution reaction, the oxygen reduction reaction, or water-splitting processes.[22−24] In addition to these, a few more review papers on TMCs revolve around the biomedical applications as in cancer therapy, antibacterial, and also photothermal therapy. Thus, the current account is relevant to introduce the scientific community to the ongoing developments and the potential of this area of research in catalysis.

2. SYNTHETIC APPLICATIONS AS A CATALYST IN CHEMICAL TRANSFORMATIONS

In a typical photocatalytic pathway, the excitation of an electron from the VB to the CB generates a hole in the former. The electron−hole pair thus generated can mediate various transformations in an independent way or in a simultaneous fashion. For instance, the electron can mediate a typical water-splitting process and the hole can mediate various oxidation reactions. Sometimes, modification of the properties by functionalization, by surface modification, by using a combination of two materials, or by the doped analogues can give superior performance as well. However, a catalyst that mediates a reaction thermally can act as either a Lewis acid (via the vacant orbital of the transition metal) or a Lewis base (via the lone pair on the chalcogenide atom).

2.1. Oxidation Reactions

Imines are an important class of organic molecules widely found in natural products, pharmaceuticals,[37] etc. The aerobic oxidation of amines to imines and nitriles was reported using MoS_x doped hollow carbon dots[38] (mechanism similar to that explained in Figure 6) and 2D-ruthenium doped MoS_2[39] as the catalyst among the various literature reports.

In 2018, our group reported the visible light promoted aerobic oxidation of aromatic amines to imines using mixed phase 2D-MoS_2 as the photocatalyst, synthesized by the lithium-intercalation method (Scheme 1).[33] The reaction was performed at 80 °C under illumination of 45 W white-light-emitting diode (LED) as the light source for 48−72 h. Moreover, the photocatalyst could be reused up to five cycles

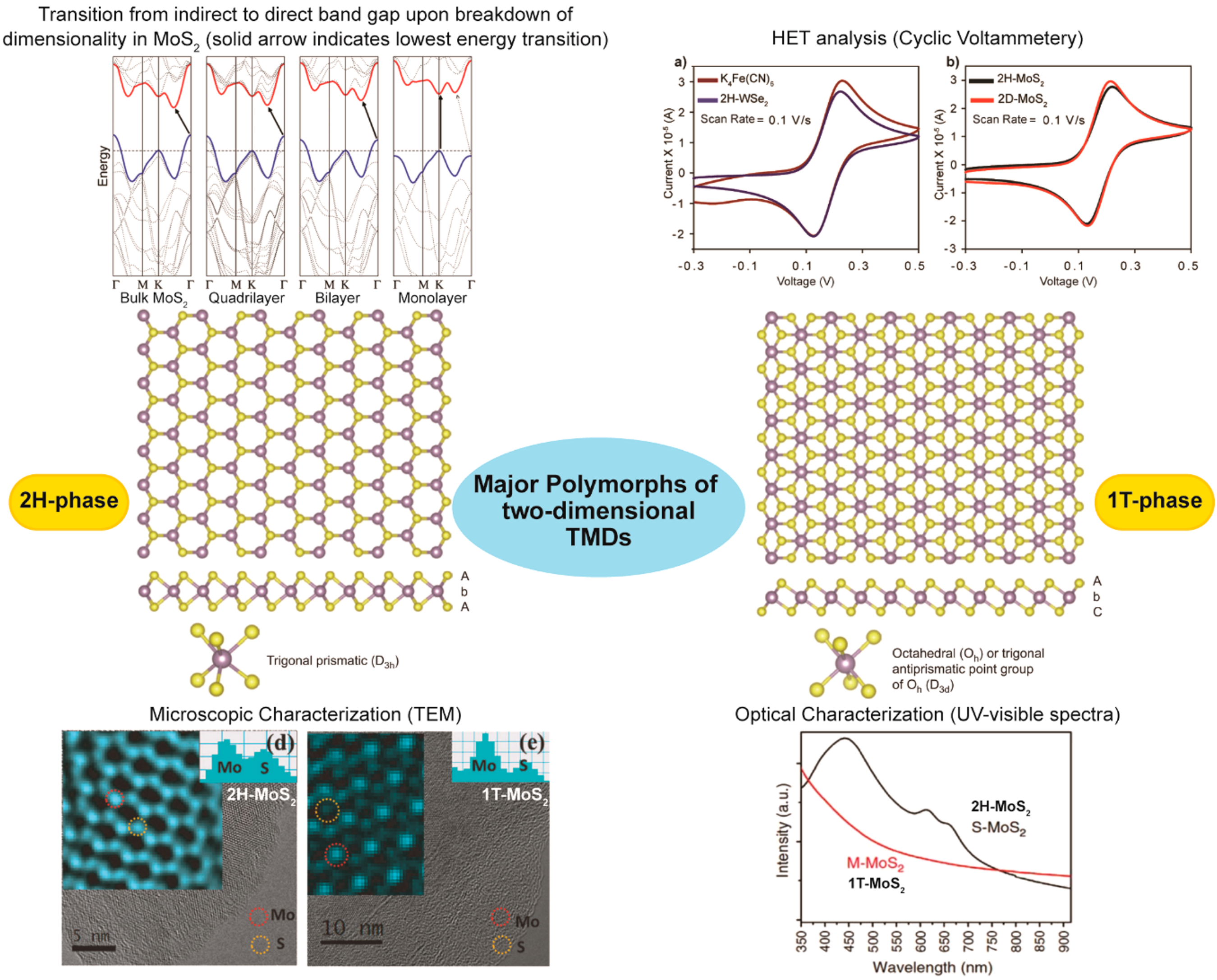


Figure 2. Schematic overview of the band gap transition and characterizations in TMDs upon breakdown of dimensionality.[8,9,18−20] Reproduced with permission from: ref 8, copyright 2020 American Chemical Society; ref 9, copyright 2013 Springer Nature; ref 18, copyright 2010 American Chemical Society; ref 19, copyright 2013 Wiley-VCH; ref 20, copyright 2016 The Authors.

with slight loss in the photocatalytic activity and showed a broad substrate tolerance.

The unmodified semiconducting nanomaterials often show low photocatalytic activity because of the recombination of the electron−hole carriers. In this regard, having metal−semiconductor or semiconductor−semiconductor heterojunctions is advantageous to usher electrons and holes in the opposite directions. The mixed phase material has the semiconducting 2H and metallic 1T phase coexisting in the same plane. Though the former acts as the generator of charge carriers, the latter provides the active site for catalysis (Figure 4).

Recently, our group carried out a comparative study of various pristine monolayered TMDs for the model aerobic coupling reaction of benzylamine to demonstrate the importance of the band gap of these materials in catalyzing organic transformations.[8] The mixed phase 2D materials were synthesized using chemical exfoliation with *n*-BuLi, and the semiconducting 2H polymorph was fabricated by solvent exfoliation using cetyltrimethylammonium bromide (CTAB) as the surfactant. They were characterized extensively microscopically and spectroscopically. Figure 5 represents some of the characterizations for the as-prepared materials.

Semiconducting 2H-WSe_2 emerged as the most suitable material for the aforesaid reaction (Scheme 2), also evident from the measurement of the band gap. Mixed phase 2D materials gave the higher conversion than the 2H analogues. This was attributed to the fact that the mixed phase materials could prevent the recombination of charge carriers effectively in contrast to the semiconducting ones. The material could be recycled up to four runs without any appreciable loss in the conversion. Cyclic voltammetry substantiates the involvement of TMDs in a HET process.

Mechanistically, in the case of mixed phase 2D-TMDs, the 2H phase generates the charge carriers via photoexcitation, after which the excited electrons are transferred to the 1T phase. However, in the absence of the metallic 1T phase, the excited electron will be directly transferred to form the superoxide radical anion. This explains the decrease in conversion for the 2H polymorph, as it cannot prevent the electron−hole recombination effectively. Benzylamine regenerates the GS of the TMD by donating an electron, thus forming the benzylamine

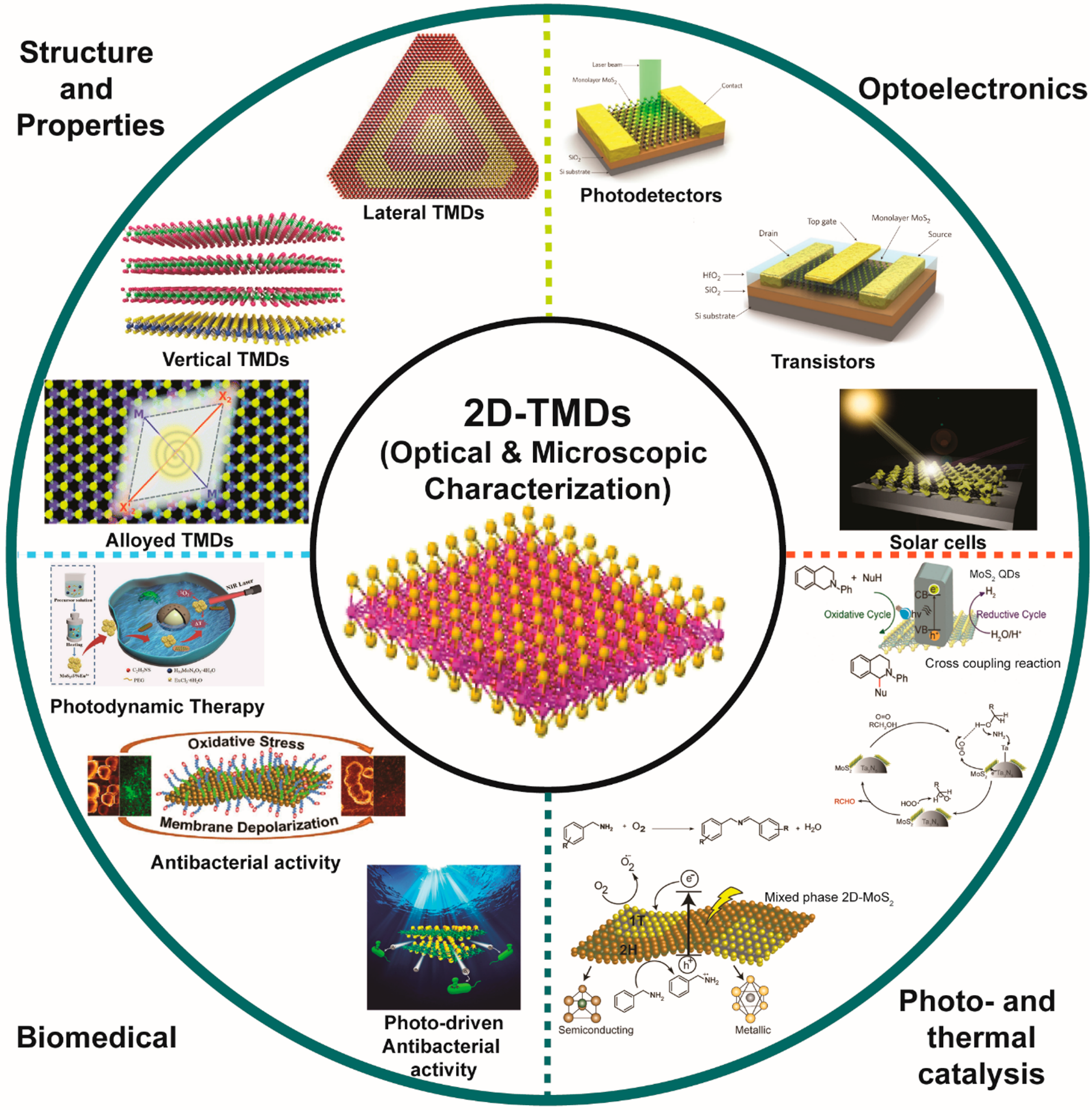


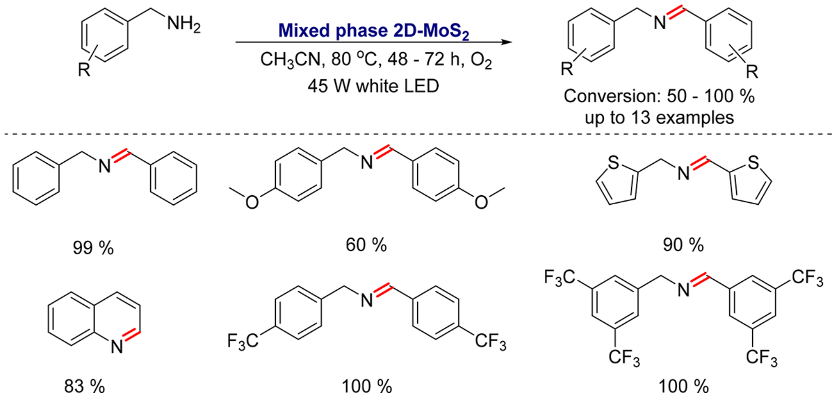
Figure 3. Potential applications of TMD-based nanomaterials over the years.[25−36] Reproduced with permission from: ref 25, copyright 2021 Elsevier; ref 26, copyright 2021 American Chemical Society; ref 27, copyright 2016 American Chemical Society; ref 28, copyright 2014 American Chemical Society; ref 29, copyright 2013 Springer Nature; ref 30, copyright 2011 Springer Nature; ref 31, copyright 2020 Springer Nature; ref 32, copyright 2015 Royal Society of Chemistry; ref 33, copyright 2018 Wiley-VCH; ref 35, copyright 2022 American Chemical Society; ref 36, copyright 2014 Royal Society of Chemistry.

radical cation $\mathbf{a}^{\bullet+}$, which forms the imine intermediate **c** and peroxide as the byproduct. Alternatively, H_2O_2 can also generate the imine **c**. The coupled product **b** is obtained upon reaction with another amine **a**. The trend in the band gap (highest for 2H-WS_2 and lowest for 2H-WSe_2) and the percentage conversion with the TMDs (highest for 2H-WSe_2 and lowest for 2H-WS_2) explain why 2H-WSe_2 emerges as the most suitable material for the transformation. The lower band gap facilitates the faster transfer of electron from the VB to the CB (Figure 6).

TMD-based materials can also be used for controlled oxidation reactions, as explained by Hao and co-workers using a $MoS_2/ZnIn_2S_4$ nanocomposite having flower-like microspheres for the semidehydrogenation of 1,2,3,4-tetrahydroisoquinoline in good yield (Scheme 3).[40]

From the mechanistic point of view, the substrate **A** is adsorbed on the surface of $ZnIn_2S_4$. The latter, upon irradiation with light generates charge carriers. The electron from the CB is transferred to MoS_2. The photogenerated hole combines with **A** to form the radical cation $\mathbf{A}^{+\bullet}$, which is followed by loss of a

Scheme 1. Aerobic Oxidation of Primary Amines to Imines by Mixed Phase 2D-MoS$_2$[a]



[a] Conversion values were obtained from GC−MS.

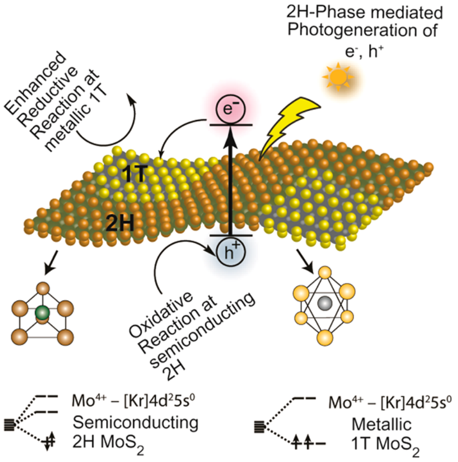


Figure 4. Separation of charge carriers in mixed phase 2D-MoS$_2$. Reproduced with permission from ref 33. Copyright 2018 Wiley-VCH.

proton to generate the radical anion **B**. The semidehydrogenated product **C** is obtained after addition of another hole and loss of a proton. The tautomerization of **C** to **D** may lead to the fully dehydrogenated product **F**; however, the process is not feasible thermodynamically over the irradiated ZnIn$_2$S$_4$ because of the less positive potential of the VB. HER takes place on the surface of MoS$_2$ (Figure 7).

The selective oxidation of alcohol is one of the most important reactions in research laboratories and industries from a synthetic point of view. A variety of oxidants such as I$_2$, H$_2$CrO$_4$, KMnO$_4$, TBHP, etc. are used as oxidizing agents. As most of them are based on Cr, Os, or Mn precursors, they are usually toxic with low selectivity and less substrate scope and often pose a threat to the environment.[41] Recently, nanomaterials have gained importance as a catalyst for oxidation reactions.[42] These include various forms of TMCs as well.

Gao et al. reported the preparation of the MoS$_2$/Ta$_3$N$_5$ nanocomposite as a heterogeneous catalyst for selective aerobic oxidation of multifunctional substrates in the presence of molecular oxygen as oxidant at 120 °C.[34] A possible mechanism involves the transfer of an electron from Ta$_3$N$_5$ NPs to MoS$_2$, which then reacts with molecular O$_2$ to generate superoxide radical anion (O$_2^{\bullet -}$). The formed superoxide radical anion interacts with the alcohol to produce the final desired aldehyde.

Recently, Chen and co-workers have synthesized 2H-MoS$_2$ material and used it as a catalyst for oxidation of 1-octanethiol to the corresponding dioctyl disulfide (Scheme 4).[43] Further, to confirm the formation of the disulfide bond, they have carried out a number of experiments and have proposed a possible mechanism. The mechanism involves the coordination of the thiol to the sulfur vacancies of 2H-MoS$_2$ surface. Subsequently, proton transfer to a S atom of 2H-MoS$_2$ NS results in detachment of the thiyl radical (RS*) from 2H-MoS$_2$ surface. Meanwhile, another thiol molecule undergoes a radical coupling resulting in the formation of organic disulfide with concomitant evolution of H$_2$ (Figure 8).

2.2. Reduction Reactions

Amines are of great importance in synthetic organic chemistry as well as in medicinal, agrochemical, and material chemistry for the synthesis of polymers.[44] Researchers have come up with strategies based on the TMD materials like a variety of MoS$_2$ catalysts, metal supported MoS$_2$, etc. for the synthesis of amines. Nitroarenes have been the most convenient starting materials for the synthesis of amines. Table S1 (Section 1, Supporting Information) presents few of the related reports in this field.

The commonly proposed mechanism for such reductive transformations involve the hydrogenation of the nitroarene, followed by a condensation reaction with the aldehyde (Scheme 5). In some cases, the imine can get hydrogenated subsequently to give the amine as demonstrated by Zhang et al. (Scheme 6).[45] The catalyst CAT-450, flower-like 2D-MoS$_2$ sheets, can be synthesized by a facile hydrothermal method followed by calcination at 450 °C. With this catalyst, a variety of nitroarenes and aromatic aldehydes give a good conversion. The material could be reused up to four cycles with good conversion and high selectivity.

Similar to the reduction of nitro compounds, TMC-based heterogeneous catalysts can also be used for the hydrogenation of unsaturated systems, including aromatic ones. Few of these are stated in Table S2 (Section 1, Supporting Information), although there are many more reports in literature pertaining to this category.

2.3. C−C and C-Heteroatom Bond-Forming Reactions

Going beyond the realms of oxidation and reduction chemistry, cross-coupling reactions[46] are the most common class of reactions for the construction of biomolecules and constitute the backbone of almost every molecule available in nature.[47] In this context, heterogeneous-material-based catalysts are relevant for the catalytic C−C and C−heteroatom bond forming

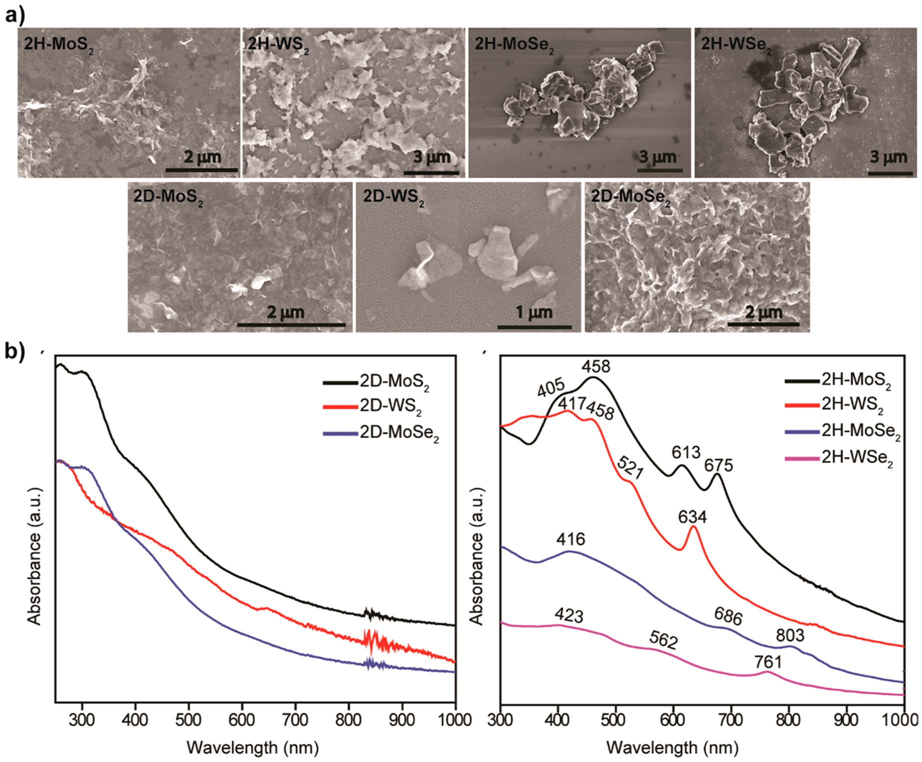
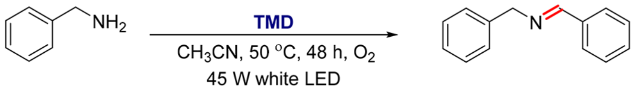


Figure 5. (a) SEM imaging showing the NSs and (b) UV−visible spectrum of all the semiconducting and mixed phase 2D-TMD materials. Reproduced with permission from ref 8. Copyright 2020 American Chemical Society.

Scheme 2. Aerobic Oxidation of Benzylamine with Various TMDs: A Comparative Study



TMD	2D-MoS$_2$	2D-WS$_2$	2D-MoSe$_2$	2H-MoS$_2$	2H-WS$_2$	2H-MoSe$_2$	**2H-WSe$_2$**
% conv. **(by GC-MS)**	50	87	73	37	32	50	**95**

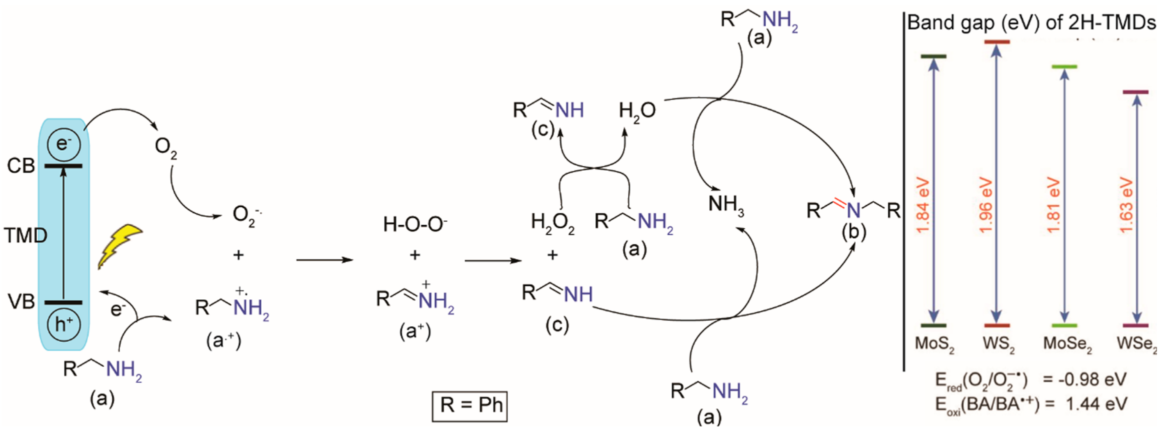
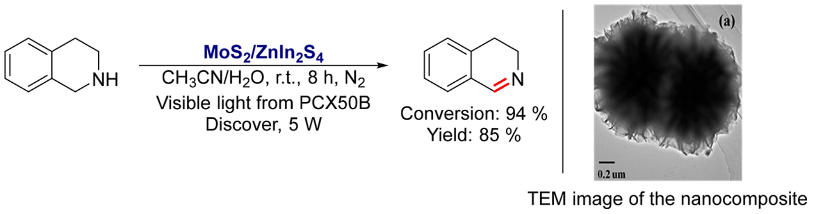


Figure 6. Plausible mechanistic pathway for the aerobic coupling reaction using layered TMDs. Reproduced with permission from ref 8. Copyright 2020 American Chemical Society.

reactions because of its atom economy, cost-effectiveness and reusability.

The homogeneous palladium catalysts are an important class of transition metal catalysts and play a pivotal role in synthetic organic chemistry for the construction of bonds.[48] Various efforts were made to synthesize cost-effective heterogeneous catalysts using limited metals or ligands for use in a benign way; for instance, Pd NPs deposited on 2H-WS$_2$ NSs[49] were

Scheme 3. Visible Light Promoted Semi-dehydrogenation of 1,2,3,4-Tetrahydroisoquinoline by $MoS_2/ZnIn_2S_4$[a]



[a] TEM image reproduced with permission from ref 40. Copyright 2019 Elsevier.

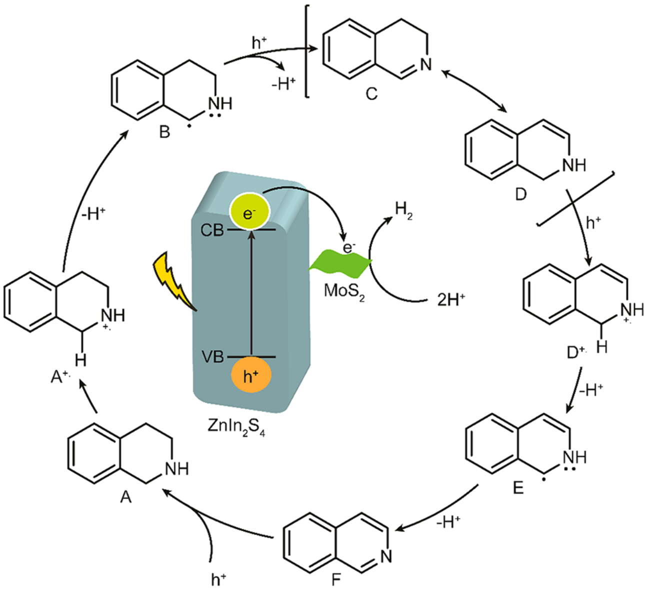
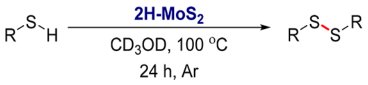
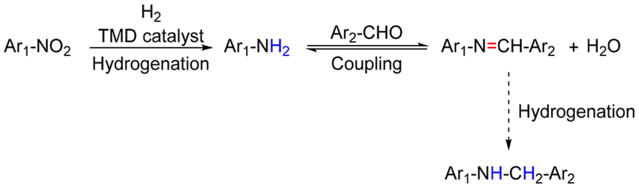


Figure 7. Plausible mechanistic pathway for the semidehydrogenation of 1,2,3,4-tetrahydroisoquinoline using $MoS_2/ZnIn_2S_4$ nanocomposite.

Scheme 4. Oxidation of Thiol by Semiconducting 2H-MoS_2



Scheme 5. Generalized Mechanism for TMD-Catalyzed Reduction of Nitroarenes to Imines and Amines



effectively used for cross-coupling reactions with aryl halides. In this case, the electrons from the CB of the photoexcited WS_2 NSs are transferred to the Pd NPs, making it electron-rich and, hence, suitable for oxidative addition with the aryl halide. Transarylation of the borate sale, followed by reductive elimination furnishes the desired coupled product.

Ji and co-workers synthesized a self-assembled 3D-Pd/MoS_2/rGO nanomaterial as a heterogeneous catalyst for Suzuki (Scheme 7a) and Heck and Sonogashira cross-coupling reactions (Scheme 7b).[50] With this catalyst, a variety of substrates could be converted to the cross-coupled product in good to excellent yields. The catalyst could be reused up to six cycles. The MoS_2 NSs prevent the restacking of rGO NSs, thus enhancing the surface area and the pore volume. This allows the leaching of the active specie, Pd, into the solution to catalyze the reaction, after which the Pd deposits on the surface of the support.

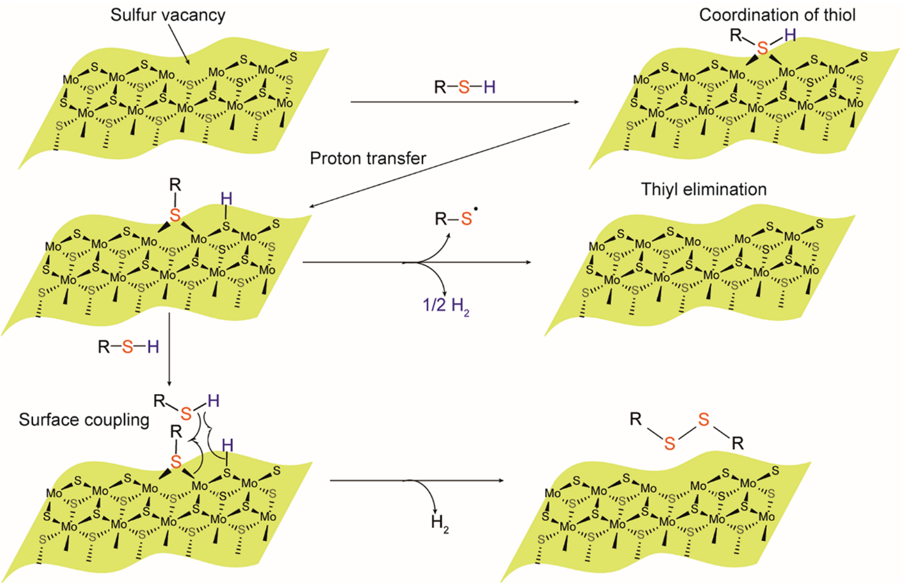
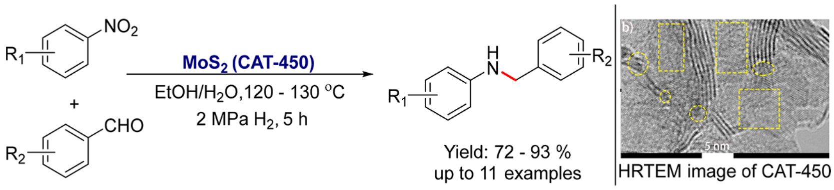


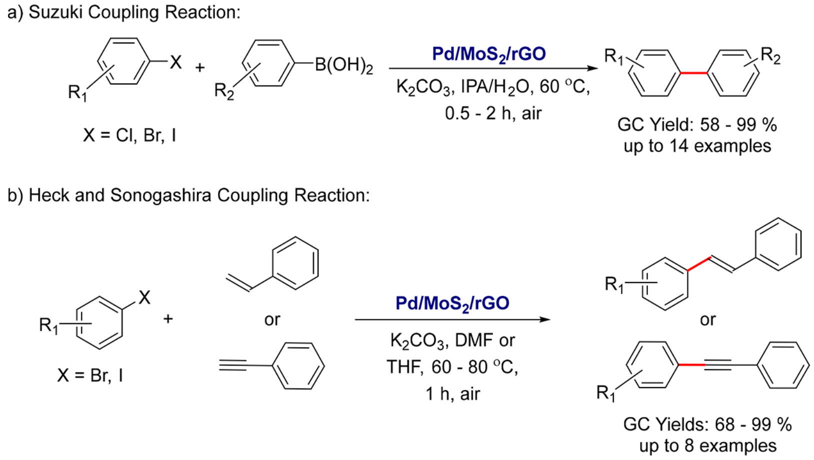
Figure 8. Proposed mechanism for 2H-MoS_2-catalyzed oxidation of thiol.

Scheme 6. Calcined 2D-MoS_2 Catalyzed One-Pot Reductive Amination of Nitroarenes[a]

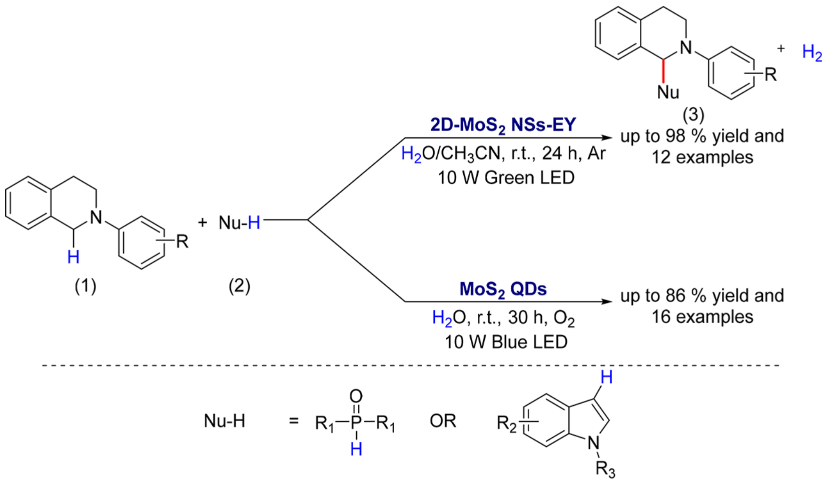


[a] TEM image reproduced with permission from ref 45. Copyright 2019 American Chemical Society.

Scheme 7. Pd/MoS_2/rGO Catalyzed Cross-Coupling Reactions



Scheme 8. Visible Light Induced 2D-MoS_2 NSs-EY and MoS_2 QDs Mediated CDC Reaction alongside HER



Our group fabricated a protocol for the visible light promoted sp^3 C−H functionalization of *N*-aryltetrahydroisoquinoline using a combination of mixed phase 2D-MoS_2 NSs and EY (Scheme 8).[16] Though the latter played the role of a catalyst, the former was used as a catalyst regenerator, thus allowing one to avoid the stoichiometric use of EY. The coupled products were obtained by reacting *N*-aryltetrahydroisoquinoline with indoles or phosphites under an argon atmosphere. The substrates bearing both electron-donating and electron-withdrawing groups on the aromatic ring are found to be effective for the CDC reaction. The strategy intended to utilize sacrificial amine donors in a typical HER to generate relevant C−C coupled products in a one-pot fashion. The catalyst was regenerated in the process and the material was found to retain activity up to two cycles because of incomplete separation of EY in subsequent runs.

Nevertheless, the use of an external photosensitizer was impetus for the transformation in most of the literature reports. Thus, our next target was to "re"-develop the above protocol without any photosensitizer. In this regard, we employed MoS_2 QDs as a photosensitizer and catalyst,[35] thus playing a dual role, for the above transformation with a similar scope, covering a range of pharmaceutically relevant molecules (Scheme 8). The hydrothermally prepared QDs (using Sodium molybdate and L-cysteine) retained its activity up to four runs.

Mechanistically, when EY is used, it will undergo an intersystem crossover (ISC) from the singlet to triplet state after excitation. The transfer of an electron from **1** to EY^{3*} generates the radical anion of EY. The mixed phase 2D-MoS_2

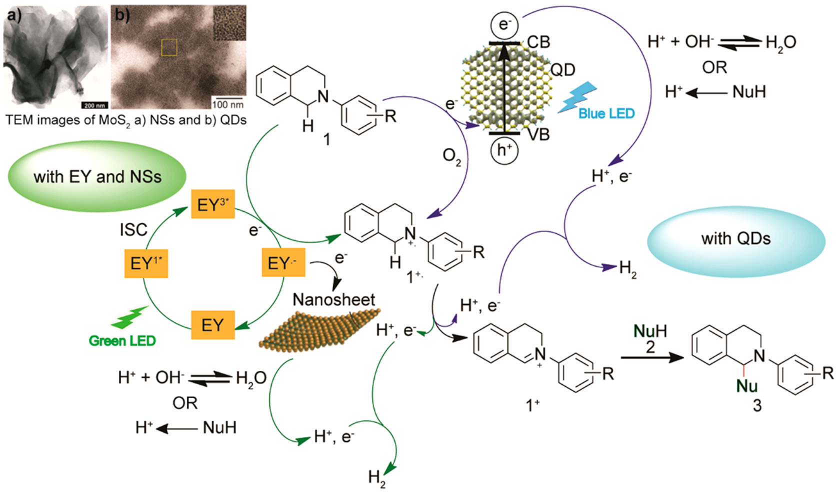
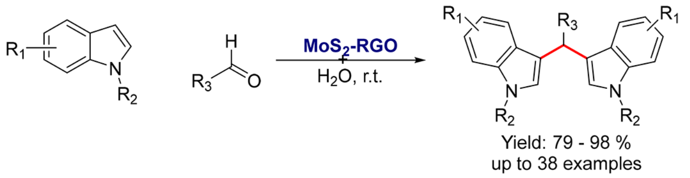


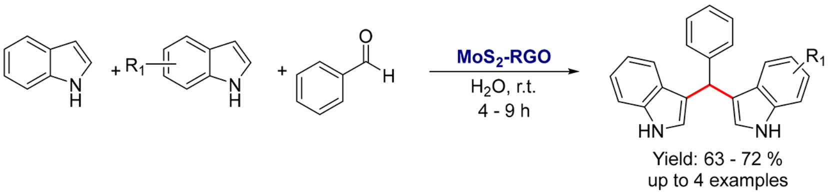
Figure 9. Mechanism of MoS_2-catalyzed CDC reaction synchronized with HER. TEM images reproduced with permission from ref 16, copyright 2019 Royal Society of Chemistry, and ref 35, copyright 2022 American Chemical Society.

Scheme 9. MoS_2-RGO Nanocomposite Catalyzed Synthesis of Bisindolylmethanes

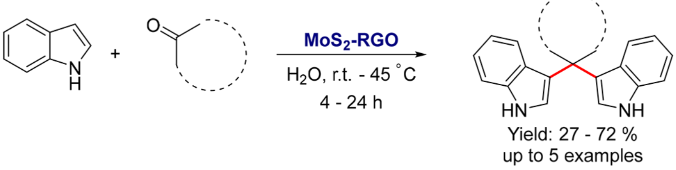
a) MoS_2 RGO nanocomposite catalyzed synthesis of bisindolylmethanes with various aldehyde and indole derivatives:



b) MoS_2 RGO nanocomposite catalyzed synthesis of unsymmetrical bisindolylmethanes:



c) MoS_2 RGO nanocomposite catalyzed ketone-derived synthesis of bisindolylmethanes:



NSs will take up this electron and transfer it for the water-splitting process that will result in HER. In the process, the GS of EY is regenerated.

However, when MoS_2 QDs are used, the excitation of an electron to the CB upon absorption of light leaves behind a hole in the VB. The GS of the QD is regenerated by the transfer of an electron from **1**. The excited electron from the CB helps in the water-splitting process followed by HER. The proton can also come from the nucleophile **2** for HER. In either case, the loss of an electron from **1** generates the radical cation $\mathbf{1}^{+\bullet}$, followed by loss of another electron and a proton to give the iminium intermediate $\mathbf{1}^{+}$, which will couple with the nucleophile **2** to give the cross-coupled product **3** (Figure 9).

A very common problem that researchers encounter while working with thiols is the auto-oxidation of the −S−H to the −S−S− bond. The construction of the thioether C−S bond instead of the disulfide S−S bond, thus, holds great significance. The nanolayered Co−Mo−S composite could be used for the purpose, as demonstrated by Sorribes et al.[51] A series of Co−Mo−S−X (X = Co/[Co + Mo] mole ratio) were prepared and screened. Co−Mo−S-0.83 emerged as the most suitable catalyst for the transformation. Further, the material displayed high chemoselectivity for the construction of the C−S bond in the presence of functionalities such as halogens, double bonds, ketones, nitriles, and carboxylic ester. The disulfide product could be reversed to the thiol precursor by the use of an excess of the alcohol analog. This explains why the C−S bond incorporated product was the major one and not the disulfide product.

Bisindolylmethanes are an important class of indole alkaloids. These are known to possess a wide range of biological applications such as anticancer activity[52] and many more. Various groups have attempted to synthesize bisindolylmethanes by electrochemical,[53] thermal,[54] and photochemical methods.[55] However, most of the methods suffer from serious

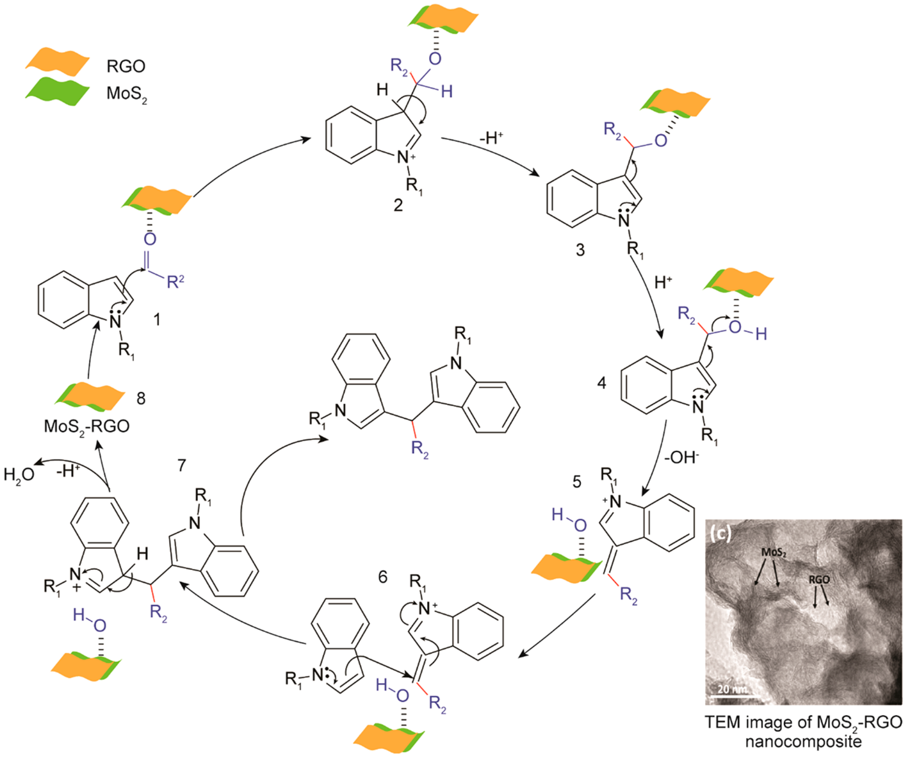
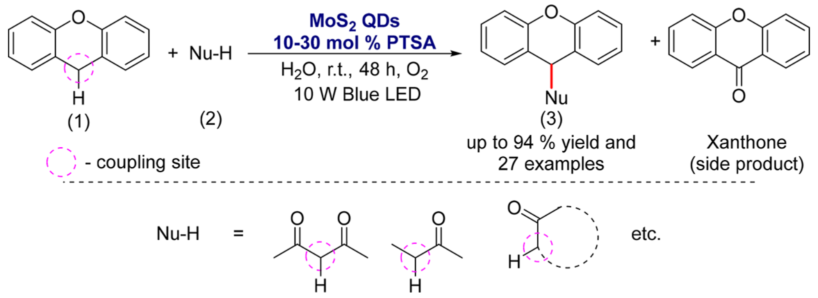


Figure 10. Mechanism for the MoS_2-RGO nanocomposite catalyzed synthesis of indole alkaloids. TEM image reproduced with permission from ref 56. Copyright 2017 American Chemical Society.

Scheme 10. Visible Light Induced MoS_2 QDs Mediated CDC Reaction of Xanthene



drawbacks such as high temperature, long reaction time, or use of commercial photocatalysts.

Recently, Bahuguna et al. have developed a heterogeneous MoS_2-RGO nanocomposite as a facile catalyst for the synthesis of indole alkaloids in a one-pot fashion in aqueous media (Scheme 9a).[56] Pristine MoS_2 and graphene oxide could not mediate the transformation well. With the composite, the scope of the reaction is broad. Further, unsymmetrical (Scheme 9b) and ketone-derived bisindolylmethanes could also be prepared by this method (Scheme 9c). The protocol is industrially relevant, as demonstrated in the gram-scale synthesis of natural products Arundine and Vibrindole.

Mechanistically, the aldehyde attaches to the surface of MoS_2 of MoS_2-RGO composite and is attacked by the third position of indole nucleophile via a Friedel–Crafts pathway to give the hydroxyalkylated intermediate **4**, which loses the hydroxyl moiety to give the enamine intermediate **5**. Finally, an attack on the electrophilic **5** by another indole moiety results in the desired bisindolylmethane product (Figure 10), setting the catalyst free for the next cycle.

Apart from the generation of the iminium ion, the MoS_2 QDs could also be employed to generate the oxocarbenium ion, as shown by our group in the coupling reactions of xanthene with a β-keto ester (Scheme 10).[57] The side product xanthone was minimized during the process of optimization. The protocol is scalable with a broad scope. Cyclic and aliphatic keto and diketo moieties were well-tolerated. Lactone and lactam did not work with the present protocol because of the less reactivity of the carbonyl center in them. The synthetic utility of the protocol was established by subjecting one of the products to Grignard addition and Wittig reaction. Moderate to good yields were obtained with excellent diastereoselectivity.

The use of DABCO (a singlet oxygen quencher) did not affect the yield and a photo energy transfer pathway could, thus, be ruled out. However, inverse kinetic solvent isotope effect was found to operate in the reaction pathway and this was attributed to the photo energy transfer process. In this case, the triplet excited state of QD, viz., QD* could transfer energy to the GS of O_2, which is the triplet form, $^3O_2$ to generate the singlet ES $^1O_2$*. The latter further undergoes SET with **1** to generate $\mathbf{1}^+$ via $\mathbf{1}^{+\bullet}$,

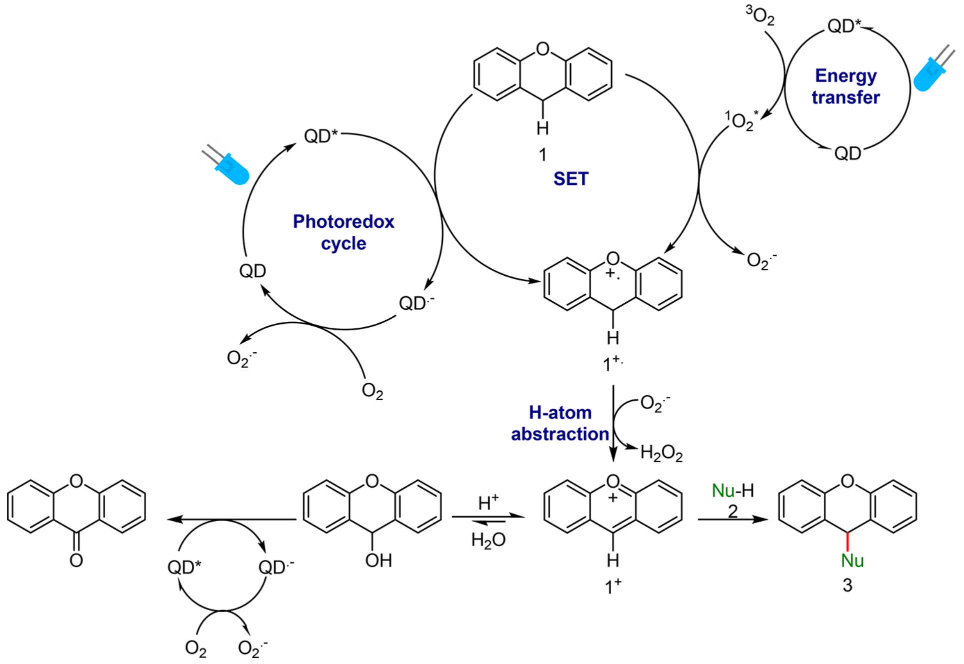


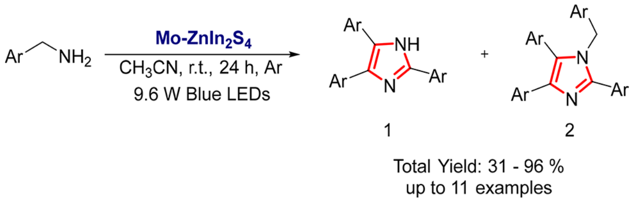
Figure 11. Mechanism for the MoS_2 QDs catalyzed CDC reaction of xanthene.

effectively because the lifetime of $^1O_2$ is higher in D_2O than H_2O (Figure 11).

From CV studies, a reductive quenching mechanism was confirmed for the QDs. The proposed mechanism is as follows. The excitation of the QD is followed by a SET with **1**, thus generating the $\mathbf{1}^{+\bullet}$ and $QD^{\bullet-}$. The reduction of O_2 to $O_2^{\bullet-}$ regenerates the GS of the QD. $O_2^{\bullet-}$ abstracts the hydrogen atom from $\mathbf{1}^{+\bullet}$ to give the oxocarbenium intermediate $\mathbf{1}^+$ along with H_2O_2. Finally, the attack by the nucleophile **2** gives the desired product **3** (Figure 11).

Another interesting scheme was proposed in 2017 using Mo−$ZnIn_2S_4$ photocatalyst for the simultaneous C−C and C−N bond formation, with concomitant cyclization (Scheme 11).[58] Two imidazole products, the tri- and the tetrasubstituted ones, were observed for most substrates.

Scheme 11. Visible Light Promoted Synthesis of Imidazoles Using Mo−$ZnIn_2S_4$ Catalyst



In the mechanism, the authors have proposed that the photoirradiation generates charge carriers that will convert benzylamine to the corresponding imine and dibenzylamine. These will subsequently form nitrogen-centered radical cations, thus regenerating the GS of the catalyst via a SET process. A proton transfer process generates the carbon-centered radicals from the nitrogen-centered radicals. The proton accepts the electron from the CB to release H_2. Concomitant C−C and C−N bond formation generates the trisubstituted (via coupling of benzylamine radicals and imine radicals) and tetrasubstituted (via coupling of dibenzylamine radicals and imine radicals) products (Figure 12).

2.4. Other Reactions

The conventional methods for transamidation or the reaction of an amide and an amine to generate another amide suffers from drawbacks such as limited scope, use of additive, expensive catalysts, etc. Recently, Zhang and co-workers have reported the transamidation reaction using MoS_2 as a catalyst (Scheme 12).[59] Various primary, secondary, and heterocyclic amines couple with amides like DMF to give the corresponding transamide products in good to excellent yields in most of the cases. The possible mechanism involves the initial coordination of MoS_2 to DMF resulting in the activation of the carbonyl group of DMF, which is subsequently attacked by the nucleophile resulting in the formation of intermediate **I**. This will further undergo proton transfer to generate the intermediate **II**. Finally, an exchange reaction between intermediate **II** and DMF results in the formation of the desired transamide product **III** (Figure 13).

TMCs have been utilized for other reactions as well. These include isomerization, ring opening, hydrodesulfurization, hydrodeoxygenation, and transamidation reactions (Section 2, Supporting Information).

3. CONCLUSION

The suitability of a material to mediate any reaction will depend on its dimensionality, morphology, band gap, functionalization, etc. A sustainable catalyst encompasses the criteria of reusability and easy economic preparation with a good yield/conversion/selectivity towards the target. Various pristine and doped forms of transition metal (Mo, W) chalcogenides (S, Se) have shown utility in synthetic organic chemistry because of their dynamic properties that impart catalytic potential. In this Account, we have highlighted the developments in this area, as well as our contributions to TMC-based catalysis. These have been summarized in Table 1 to provide a brief overview.

In addition, there are some other reports as well in this category. However, the field is still in its infancy, as there are

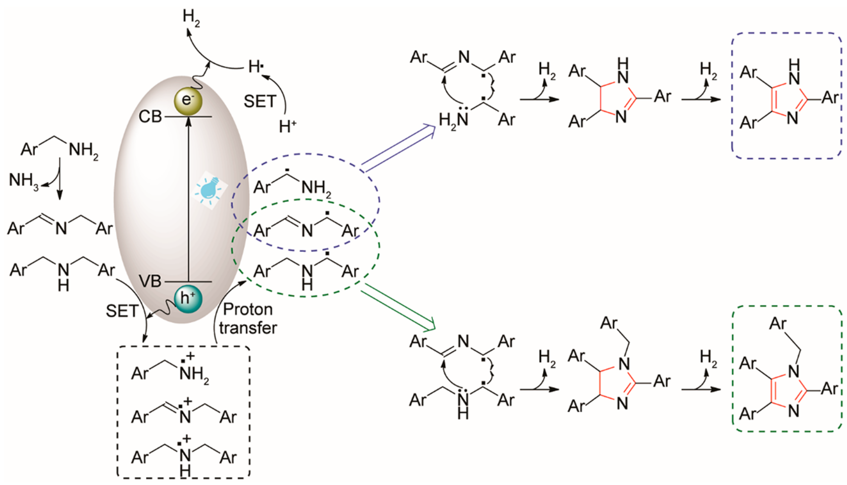
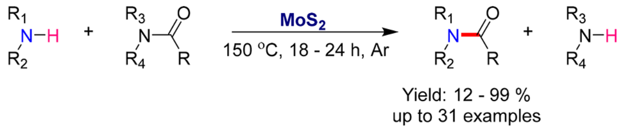


Figure 12. Proposed mechanism for the synthesis of imidazoles using Mo−ZnIn$_2$S$_4$ catalyst.

Scheme 12. Transamidation Reaction Catalyzed by MoS$_2$



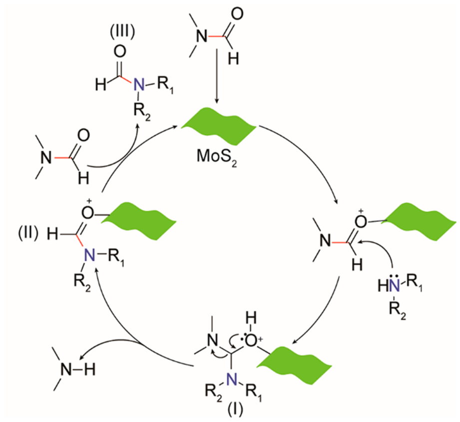


Figure 13. Mechanism of transamidation reaction catalyzed by MoS$_2$.

certain challenges that need to be overcome in the following aspects (Figure 14).

(1) One of the challenges for current researchers in the field is to develop catalysts towards enantioselective/diastereoselective transformations, because such reactions often constitute crucial step(s) in drug design and natural product synthesis. This is one of the most sought upon aspect in this area of research and its development will enhance the utility of this field manifold. Such chiral catalysts can be possibly obtained by modifying the surface with chiral ligands or complexes and, also, by preparation of chiral nanoparticles. The enantioselectivity can be achieved either through the generation of a chiral environment or by the selective absorption of chiral substrate. This approach has already been established with various other nanomaterials but never done with TMCs.[60,61]

(2) Multicomponent reactions (MCRs) are an important class of reactions because of their atom-economic approach. Though this approach has been well adopted in organic catalysis, there are no reports pertaining to nanomaterial mediated MCRs. Not only the TMC-based materials but also other nanomaterial-based catalyst can also be used to enhance the efficacy of the process even more.

(3) Metal-complex-based stabilization of organic reactive intermediates is a key step in many organic transformations. For example, carbenes are very unstable but highly important intermediates for many synthetic transformations that can be stabilized by using a ruthenium-based complex. Similarly, TMC-based nanomaterials can be used for stabilization of various reactive intermediates such as carbene, radical, carbocation, etc. through metal coordination. Hence, one may also be tempted to envision TMC-stabilized carbenes, etc. as sustainable alternatives to the former.

(4) To date, the use of multiple catalysts in a transformation is restricted to the use of mostly two nanomaterials in a given system (dual catalysis). However, one can also merge the efficacy of small molecule homogeneous organic catalysts with the heterogeneity of nanomaterials. This would typically involve a modification of the nanomaterial surface with the organic catalyst (for instance, Ru- or Ir-based catalyst). The approach seems promising and will go a long way in bringing together the areas of nanomaterials and catalysis even more.

(5) Despite the presence of a few reports on the doping of these materials, a lot more work needs to be done to control the extent or amount of doping. The band gap and other properties will also change with the level of doping and this, in turn, will affect the catalytic activity.

(6) Although various mechanisms are proposed for the organic transformations mediated by TMCs or their analogues, it is necessary to establish methods for a detailed analysis or study of the same. This will also help one to design other reactions by fundamentally understanding the behavior of the material in a given environment.

(7) An important challenge in this field is to theoretically correlate the structure, properties, and activity of a given material for an organic transformation. This will also validate the experimental output. Such an approach has proved to be fruitful for small molecule catalysis,

Table 1. TMCs in Organic Transformations: An Overview

sl. no.	type of chalcogenide	reaction type	substrate	product	ref
1	MoS_x doped hollow carbon dots	oxidation	mostly aryl amines and few aliphatic amines	imines	38
2	2H-WSe_2 NSs				8
3	mixed phase 2D-MoS_2 NSs				33
4	2D-ruthenium doped MoS_2 sheets			nitriles	39
5	$MoS_2/ZnIn_2S_4$ microspheres	oxidation/semidehydrogenation	1,2,3,4-tetrahydroisoquinoline	3,4-dihydroisoquinoline	40
6	MoS_2/Ta_3N_5 nanocomposite	oxidation	alcohols	aldehydes	34
7	2H-MoS_2 NSs		1-octanethiol	dioctyl disulfide	43
8	2D-MoS_2 sheets	reduction	nitroarenes	amines	45
9	Pd NPs deposited on 2H-WS_2 NSs	Suzuki reaction	aryl halides	biaryls	49
10	3D-Pd/MoS_2/rGO composite	Suzuki, Heck, and Sonogashira coupling reactions		biaryls, disubstituted alkenes and alkynes	50
11	mixed phase 2D-MoS_2 NSs-EY	$C(sp^3)-C(sp^2)$ CDC coupling	*N*-aryltetrahydroisoquinoline with indoles/phosphites	C−C coupled products	16
12	MoS_2 QDs		xanthene with β-keto esters		35
13	MoS_2 QDs				57
14	Co−Mo−S composite	cross-coupling	thiols	C−S coupled products	51
15	MoS_2-RGO nanocomposite		aldehydes with indoles	bisindolylmethanes	56
16	Mo−$ZnIn_2S_4$ composite	C−C and C−N bond formation	arylamines	imidazoles	58
17	MoS_2 NSs	transamidation	amines with amides	transamide	59

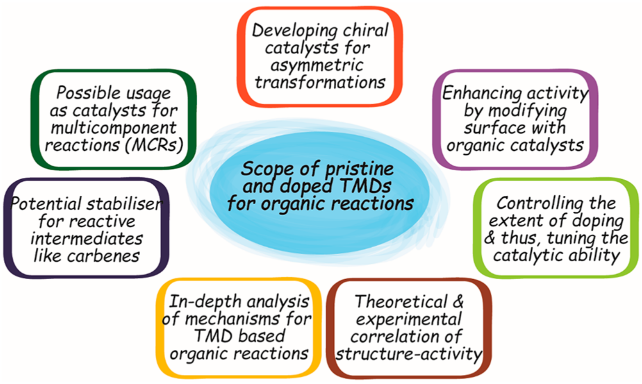


Figure 14. Scope of TMC and related materials in the field of organic catalysis and transformations.

especially during the optimization process for a given transformation.

Despite the aforesaid challenges, we strongly believe that this field will grow immensely in the near future because of its strong practical applicability and inexhaustible potential in the scientific and industrial sectors.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/accountsmr.2c00110.

Tables of catalysts and details of other reactions (PDF)

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Author Contributions

The manuscript was written through the contributions of all the authors. All authors have given approval to the final version of the manuscript.

Author Contributions

[#]K.J. and Y.R.G. contributed equally.

Funding

The authors thank SERB (CRG/2020/001197) for financial support.

Notes

The authors declare no competing financial interest.

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Komal Jaiswal obtained her B.Sc. (Chemistry Honours) degree from St. Xavier's College, Calcutta and M.Sc. from Indian Institute of Science (IISc) Bangalore. Currently, she is carrying out her doctoral studies under the supervision of Prof. Mrinmoy De at the Department of Organic Chemistry, IISc, Bangalore. Her work revolves around the development of synthetic or catalytic strategies (mainly photo-mediated) with materials of various dimensionality and band gap.

Yarabahally R. Girish obtained his undergraduate and postgraduate degree from Bangalore University. He pursued his doctoral studies at the University of Mysore. Subsequently, he continued with his postdoctoral work in Prof. Mrinmoy De's group at the Department of Organic Chemistry, IISc, Bangalore and, then, at Adichunchanagiri University. Currently, he works as an Assistant Professor at the School of Natural Sciences, Adichunchanagiri University, Karnataka. His interest is based on catalysis using two-dimensional materials.

Mrinmoy De received his M.Sc. from Indian Institute of Technology, Bombay, and his Ph.D. from University of Massachusetts at Amherst under the supervision of Prof. Vincent M. Rotello and was a CCNE and NSEC postdoctoral fellow at Northwestern University. Since 2014, Prof. De has been at the Indian Institute of Science, Bangalore, where he is an associate professor at department of organic chemistry. His research focuses on the preparation various nanomaterials and their application to photocatalysis and biological systems.

■ ACKNOWLEDGMENTS

K.J. thanks PMRF for doctoral fellowship.

■ ABBREVIATIONS

TMDs	transition metal dichalcogenides
TMCs	transition metal chalcogenides
2D/3D	two dimensional/three dimensional
HET	heterogeneous electron transfer
SET	single electron transfer
rt	room temperature
GR	graphene
rGO/RGO	reduced graphene oxide
HDS	hydrodesulfurization
HDO	hydrodeoxygenation
DMF	*N*,*N*-dimethylformamide
CDC	cross dehydrogenative coupling
HER	hydrogen evolution reaction
CB	conduction band
VB	valence band
GS	ground state
ES	excited state
QDs	quantum dots
NPs	nanoparticles
NSs	nanosheets
EY	eosin Y

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