Superlattices of covalently cross-linked 2D materials for the hydrogen evolution reaction

Cite as: APL Mater. 8, 020902 (2020); https://doi.org/10.1063/1.5135340
Submitted: 05 November 2019 . Accepted: 14 January 2020 . Published Online: 03 February 2020

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Note: This paper is part of the Special Issue on New Perspectives on Emerging Advanced Materials for Sustainability.

ABSTRACT
Amongst the recent developments in 2D materials, van der Waals heterostructures formed by depositing a monolayer or few-layers of a 2D material on a monolayer or on few-layers of the same or another 2D material have attracted great attention. As an alternative to such heterostructures, we have carried out investigations on covalently cross-linked heterostructures by chemical coupling of layers of the same or different 2D materials. This effort has met with success, with typical systems studied by us being graphene–graphene, graphene–MoS$_2$, C$_3$N$_4$–MoS$_2$, borocarbonitride–MoS$_2$, and phosphorene–MoS$_2$. We describe these structures to demonstrate how the covalent cross-linking strategy yields novel 2D nanocomposites. These structures exhibit interesting gas adsorption properties as well as noteworthy hydrogen evolution reaction (HER) activity. The phosphorene–MoS$_2$ nanocomposite is found to exhibit superior photocatalytic HER activity. The most interesting nanocomposite is BCN–MoS$_2$ which exhibits electrochemical HER activity comparable to platinum, thus providing a new and novel example of metal-free catalysis.

I. INTRODUCTION
There has been intense research on 2D materials in the last few years. Besides graphene and other elemental 2D materials, intense investigations have been carried out on other inorganic 2D materials such as transition metal dichalcogenides. In particular, MoS$_2$ has been found to exhibit many novel properties, an interesting one pertaining to the hydrogen evolution reaction (HER). A significant development in the area of 2D materials is that of van der Waals heterostructures obtained by the stacking of different 2D structures. Typical of these heterostructures are graphene–MoS$_2$ and graphene–BN. Another interesting development relates to the generation of novel materials by covalent cross-linking of 2D layers. Examples of these are graphene–graphene, graphene–MoS$_2$, MoS$_2$–C$_3$N$_4$, MoS$_2$–borocarbonitride (BCN), phosphorene–MoS$_2$ (P–MoS$_2$), phosphorene–C$_3$N$_4$ (P–C$_3$N$_4$), and phosphorene–BCN (P–BCN) nanocomposites by employing coupling reactions and their photo/electrocatalytic H$_2$ evolution activities. The choice of 2D MoS$_2$, BCN, and C$_3$N$_4$ to generate these new composites was based on the known catalytic and other properties of these materials relevant to HER studies reported in the literature. The choice of phosphorene was based on the expectation that the lone pairs on phosphorus may interact with a direct bandgap semiconductor such as 2H-MoS$_2$ to give rise to novel properties. Photocatalytic H$_2$ evolution with the P–MoS$_2$ nanocomposite is indeed found to...
be substantial with an evolution of 25 734 μmol h⁻¹ g⁻¹. More interestingly, the BCN–MoS₂ nanocomposite shows outstanding electrochemical HER activity with a Tafel slope of 33 mV dec⁻¹ close to that of Pt. We have also given an account of the effect of the relative proportions of the two 2D layers in the nanocomposites and of the length of the linker (inter-layer gap) on the HER activity of the covalently linked 2D nanocomposites.

II. DIFFERENT COVALENTLY CROSS-LINKED 2D MATERIALS

Sonogashira coupling has been employed in synthetic organic chemistry to form carbon–carbon bonds between a terminal alkene and an aryl or a vinyl halide. By this means, conjugated microporous polymers (CMPs) are obtained which display interesting morphological and functional properties. We have employed Sonogashira coupling to prepare nanocomposites based on several 2D layered materials including graphene and MoS₂. The list of reactants employed and the covalently linked nanocomposites obtained by us by means of Sonogashira coupling are presented in Table I.

In Scheme 1, we show how covalently cross-linked graphene–graphene nanocomposites are obtained by Sonogashira coupling. The preparative method involves iodobenzene functionalization of reduced graphene oxide (RGO–IBz) with the in situ prepared diazonium salt of 4-iodoaniline. The subsequent steps involve dispersing RGO–IBz in dry N,N-dimethylformamide (DMF) by sonication. The RGO–IBz sheets in the dispersion are cross-linked with the 1,4-diethynylbenzene or 4,4′-diethynylbiphenyl linker in the presence of Pd(0) and Cu(+) catalysts to obtain the 3D graphene frameworks (PGF-1 and PGF-2).

We have extended the Sonogashira coupling strategy to prepare MoS₂–MoS₂ and MoS₂–RGO nanocomposites. Scheme 2 presents the steps involved in preparing covalently pillared MoS₂ and MoS₂–RGO nanocomposites. Metallic 1T-MoS₂ was prepared by lithium intercalation in 2H-MoS₂ followed by exfoliation. The process of Li-intercalation and exfoliation results in excess negative charge to the overall neutral structure which is distributed over the exterior S atoms. Iodobenzene-functionalized MoS₂ (MoS₂–IBz) was prepared by treating exfoliated MoS₂ with the diazonium salt of 4-iodoaniline. The functionalization reaction is facilitated by an electron transfer from the metallic 1T-MoS₂ to the electrophilic diazonium salt of 4-iodoaniline precursor to form C–S bonds. Further steps involve obtaining the MoS₂–IBz dispersion in dry DMF by sonication and cross-linking it with the 4,4′-diethynylbiphenyl (DEBP) linker in the presence of Pd(0) and Cu(+) salts. The synthetic process for the MoS₂–RGO composite is similar to that of the MoS₂–MoS₂ nanocomposites except for the initial reduction of graphene oxide (GO) in hydrate hydrate to yield reduced graphene oxide (RGO). Prior to the coupling, MoS₂–IBz and RGO–IBz were mixed and dispersed in dry DMF through sonication.

In order to prepare C₃N₄–NRGO and C₃N₄–MoS₂ nanocomposites, we have adopted the carbodiimide cross-linking strategy using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) as the coupling reagent (Scheme 3). The list of the reactants employed and the cross-linked products obtained by this are given in Table II. The C₃N₄–NRGO nanocomposite was obtained by reacting amine-functionalized C₃N₄ with nitrogen-doped reduced graphene oxide (NRGO), prepared by the microwave irradiation of a mixture of graphene oxide (GO) and urea, in the presence of EDC. To prepare C₃N₄–MoS₂ nanocomposites, amine-containing C₃N₄ layers were treated with carboxylate-functionalized MoS₂ in

### Table I. Reactants employed to generate nanocomposites by Sonogashira coupling

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Covalently cross-linked products</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO–IBz</td>
<td>PGF-1²⁵ c</td>
</tr>
<tr>
<td>1,4-diethynylbenzene</td>
<td></td>
</tr>
<tr>
<td>RGO–IBz</td>
<td>PGF-2²⁵ c</td>
</tr>
<tr>
<td>4,4′-diethynylbiphenyl</td>
<td></td>
</tr>
<tr>
<td>MoS₂–IBz</td>
<td>MoS₂–MoS₂³⁷⁶</td>
</tr>
<tr>
<td>4,4′-diethynylbiphenyl</td>
<td></td>
</tr>
<tr>
<td>MoS₂–IBz</td>
<td>MoS₂–RGO³⁷⁶</td>
</tr>
<tr>
<td>RGO–IBz</td>
<td>MoS₂–NRGO³⁷⁶</td>
</tr>
<tr>
<td>4,4′-diethynylbiphenyl</td>
<td></td>
</tr>
</tbody>
</table>

² Tetakis(triphenylphosphine) palladium(0), [Pd(PPh₃)₄], and copper(I) iodide (CuI) were used as catalysts. Triethylamine (Et₃N) was used as the base in N,N-dimethylformamide (DMF) medium in all the reactions.
³ Iodobenzene functionalized (IBz) RGO and MoS₂, are represented as RGO–IBz and MoS₂–IBz, respectively.
⁴ PGF stands for pillared graphene frameworks.
SCHEME 2. Synthesis of covalently bonded MoS$_2$–MoS$_2$ and MoS$_2$–RGO nanocomposites through Sonogashira coupling. Various steps involves the following: (a) reaction of bulk MoS$_2$ with n-butyllithium followed by exfoliation to obtain metallic 1T-MoS$_2$, (b) reduction of graphene oxide with hydrazine hydrate, [(c) and (g)] iodobenzene functionalized MoS$_2$ and RGO, and [(d) and (h)] MoS$_2$ and MoS$_2$–RGO assemblies. Reproduced with permission from Pramoda et al., J. Mater. Chem. A 4, 8889 (2016). Copyright 2016 The Royal Society of Chemistry.

TABLE II. Reactants employed to generate nanocomposites by EDC coupling.¹

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Covalently cross-linked products</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃N₄–NH₂ b, NRGO–COOH f</td>
<td>C₃N₄–NRGO g</td>
</tr>
<tr>
<td>C₃N₄–NH₂ b, MoS₂–CH₂COOH d</td>
<td>C₃N₄–MoS₂ i</td>
</tr>
<tr>
<td>BCN–NH₂ e, BCN–COOH f</td>
<td>GBN/BCN–MoS₂¹ l</td>
</tr>
<tr>
<td>MoS₂–CH₂NH₂ f, BCN–COOH f</td>
<td>G/BCN–MoS₂¹ k</td>
</tr>
<tr>
<td>MoS₂–CH₂COOH f, BCN–NH₂ f</td>
<td>BN/BCN–MoS₂¹ k</td>
</tr>
</tbody>
</table>

¹N-(3-dimethylaminopropyl)-N’-ethylcarbodiimidehydrochloride (EDC·HCl) and 1-hydroxybenzotriazole (HOBt) were used as coupling agents with N,N-diisopropylethylamine (DIPEA) as a base in the N,N-dimethylformamide (DMF) medium for all the reactions.

²Amine group containing carbon nitride (C₃N₄–NH₂).

³Acid functionalized nitrogen doped reduced graphene oxide (NRGO).

⁴Acid functionalized molybdenum disulfide (MoS₂–CH₂COOH).

⁵Amine group containing BN domains of BCN (BCN–NH₂).

⁶Amine functionalized MoS₂ (MoS₂–C₆H₄NH₂).

⁷Graphene–BN domain connected BCN assemblies.

⁸Acid functionalized MoS₂ (MoS₂–CH₂COOH).

⁹BN domain cross-linked BCN–MoS₂ nanocomposites (BN/BCN–MoS₂).

The presence of the EDC reagent. Carboxylate-functionalized MoS₂ (MoS₂–CH₂COOH) was obtained by the reaction of metallic 1T-MoS₂ with bromoacetic acid.¹² Metallic 1T-MoS₂, possessing excess electrons on the surface, behaves as a nucleophile and undergoes substitution of the bromo group in bromoacetic acid by the sulfur of MoS₂, thereby forming the C–S bond.

The scheme for linking the graphene domains in a BCN with each other (GG/BCN–BCN) and for linking the graphene domains with the BN domains in BCN (GBN/BCN–BCN) is presented in Scheme 4.²⁰

Linking graphene domains in BCN with each other (GG/BCN–BCN) was accomplished by bonding the carboxyl functional groups of the graphene domain of one BCN layer with the hydroxyl groups of the graphene domain of another BCN layer using the esterification strategy.²¹,²² Carboxyl functional groups of the graphene domains on cross-linking with amine groups of the BN domain using the EDC reagent yield nanocomposites of graphene with BN domains (GBN/BCN–BCN).²³

In Scheme 5, we show graphene as well as BN domain in BCN covalently linked to MoS₂ by carbodiimide coupling.

1T-MoS₂ nanosheets generated by lithium intercalation of bulk 2H-MoS₂,²³,²⁶ are reacted with a 10-fold excess of iodoaniline (I–C₆H₄–NH₂) to obtain amine functionalized MoS₂ (MoS₂–C₆H₄NH₂).²⁷ Subsequently, the surface amine groups on MoS₂ are reacted with residual carboxyl functional groups of BCN in the presence of the EDC reagent to yield G/BCN–MoS₂.²¹ Coupling of the acid functionalized MoS₂ (MoS₂–CH₂COOH), obtained by the reaction of 1T-MoS₂ with bromoacetic acid,²² with the amine groups on BCN yields BN/BCN–MoS₂ nanocomposites. Similarly, we have prepared G/BCN–MoSe₂ and BN/BCN–MoSe₂ by cross-linking amine functionalized MoSe₂ (MoSe₂–C₆H₄NH₂) and acid functionalized MoSe₂ (MoSe₂–CH₂COOH), respectively.
utilizing residual carboxyl and amine functional groups of BCN, respectively.  

For the synthesis of P–C₃N₄ and P–BCN nanocomposites, we initially prepared few-layer phosphorene by exfoliating black phosphorus in anhydrous DMF solvent. The reaction of phosphorene with the bromoacetic acid reagent gives carboxylic acid-functionalized phosphorene (P–CH₂COOH). 27 Reactions of P–CH₂COOH with amine functionalized C₃N₄ as well as BCN were carried out in the presence of EDC·HCl to obtain P–C₃N₄ and P–BCN nanocomposites, respectively. Here, the condensation reaction between the carboxyl and amine groups leads to the formation of the amide bond. Covalently linked P–C₃N₄ and P–BCN nanocomposites have been reported for the first time in the present study.

### III. GAS ADSORPTION PROPERTIES IN BRIEF

Some of the covalently linked 2D nanocomposites have been examined for gas adsorption properties since the parent 2D materials themselves are known to show good gas adsorption properties. For example, graphene 2 and BCN 12 exhibit high surface areas. Furthermore, we considered it possible that the surface properties may have some effect on the HER activity. Nitrogen adsorption isotherms of covalently linked graphene frameworks (PGFs) display characteristics of both type-I and type-II features in the low and high pressure sections, respectively, following the IUPAC system. 15,30 The Brunauer–Emmet–Teller (BET) surface areas of PGF-1 and PGF-2 are ~770 m²/g and 820 m²/g, respectively. The higher N₂ uptake by PGF-2 shows the effect of increasing the pillar length from the 1,4-diethynylbenzene to 4,4′-diethynylbiphenyl linker.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>Surface area (m²/g)</th>
<th>H₂ uptake (wt. %, 77 K, 1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium-organic frameworks</td>
<td>1441</td>
<td>1.0</td>
</tr>
<tr>
<td>Triazolate-bridged MOFs</td>
<td>1770</td>
<td>. . .</td>
</tr>
<tr>
<td>Graphene oxide frameworks</td>
<td>470</td>
<td>1.2</td>
</tr>
<tr>
<td>Graphene frameworks</td>
<td>550</td>
<td>0.5</td>
</tr>
<tr>
<td>PGF-1</td>
<td>820</td>
<td>1.2</td>
</tr>
<tr>
<td>PGF-2</td>
<td>770</td>
<td>1.0</td>
</tr>
</tbody>
</table>

PGF-1 and PGF-2 exhibit CO₂ uptakes of 572 ml/g and 301 ml/g corresponding to 112 wt. % and 60 wt. %, respectively, at 195 K and 1 atm. Under ambient conditions (273 K and 1 atm), PGF-1 and PGF-2 exhibit CO₂ uptakes of ~7.2 wt. % and 6.3 wt. %, respectively. PGF-1 and PGF-2 show H₂ uptakes of 1.2 wt. % and 1.0 wt. %, respectively, at 1 atm and 77 K. These values are comparable with high surface area MOFs 1,31 and with some of the graphene-based frameworks 32,33 (Table III).

The N₂ sorption profiles of MoS₂–MoS₂ and MoS₂–RGO (3:1) nanocomposites show adsorption characteristics similar to the PGFs with BET surface areas of ~498 m²/g and 512 m²/g, respectively. 18,30 Covalently linked MoS₂–MoS₂ and MoS₂–RGO (3:1) nanocomposites show CO₂ uptakes of 11.4 wt. % and 12.8 wt. %, respectively, at 298 K and 1 atm. The high CO₂ uptake of these
nanocomposites is attributed to the interaction of the CO₂ molecule with the π-electron cloud of the aromatic network as well as with sulfur defects in MoS₂.⁷⁻¹⁰ Even though the uptake efficiency of CO₂ is less than that of some of the reported MOFs and zeolite 13 X,¹⁷⁻²⁰ these assemblies can be useful in harsh chemical and thermal environments.

IV. HER ACTIVITY

MoS₂–MoS₂ and MoS₂–RGO nanocomposites: The photocatalytic HER activity of MoS₂–MoS₂ and MoS₂–RGO nanocomposites has been examined in the presence of Eosin Y (EY) dye as the sensitizer and triethanolamine (TEOA) as the sacrificial electron donor, under UV-vis light (halogen lamp, 100 W) illumination. In Fig. 1(a), we show the yields of H₂ obtained with MoS₂–MoS₂ and MoS₂–RGO nanocomposites as well as with the starting MoS₂–IBz. MoS₂–IBz displays an activity of only 68 μmol g⁻¹ h⁻¹ [turnover frequency (TOF), 0.01 h⁻¹], whereas the covalently linked MoS₂–MoS₂ nanocomposite shows an enhanced activity of 1752 μmol g⁻¹ h⁻¹ (TOF of 0.84 h⁻¹). The improved activity in the case of the covalently linked MoS₂–MoS₂ nanocomposites is due to the increased surface area as well as the greater exposed edge sites of MoS₂ due to cross-linking. This is corroborated by the fact that MoS₂–MoS₂ nanocomposites (498 m² g⁻¹) show ~16× enhancement in surface area compared with the starting few-layer MoS₂ (30 m² g⁻¹). Second, theoretical and experimental investigations have shown that the catalytic HER activity of 2D MoS₂ is solely dependent on the edge sites because the in-plane sites are inert.

In covalently linked composites, the MoS₂ edge sites are more exposed due to pillaring which gives rise to a high active surface area for H⁺ adsorption and contributes to the enhanced activity. The MoS₂–RGO (3:1, 2:1, 1:1) nanocomposites exhibit HER catalytic activities of 1384 μmol g⁻¹ h⁻¹, 1307 μmol g⁻¹ h⁻¹ and 350 μmol g⁻¹ h⁻¹, respectively, demonstrating that the activity increases with the MoS₂ content. On the other hand, starting MoS₂–IBz exhibits an activity of only 68 μmol g⁻¹ h⁻¹, while RGO alone does not show any notable H₂ evolution. These results show that in these nanocomposites, MoS₂ is the active component for H₂ production, while RGO facilitates electron transfer to the active sites in the 3D network.

G/BCN–MoS₂ and BN/BCN–MoS₂: We have examined the visible-light induced HER activity of G/BCN–MoS₂ and BN/BCN–MoS₂ composites in an aqueous medium containing TEOA as the sacrificial electron donor and EY dye as the photosensitizer. The yields of H₂ with cross-linked BN/BCN–MoS₂ and G/BCN–MoS₂ (1:2) nanocomposites and the respective physical mixtures are presented in Fig. 1(b).¹¹ MoS₂–CH₂COOH and BCN exhibit activities of 1663 μmol h⁻¹ g⁻¹ and 136 μmol h⁻¹ g⁻¹, respectively. In the case of BN/BCN–MoS₂ (1:2) and G/BCN–MoS₂ (1:2) nanocomposites, we observe ~5× improvement in photocatalytic HER activity with respect to MoS₂, whereas the physical mixture of BCN and MoS₂ shows only ~2× enhancement [Fig. 1(b)]. Clearly, covalently linked BCN and MoS₂ layers exhibit higher HER activity compared to the physical mixture due to the distinctive 3D heterolayer network along with the presence of microporous channels which offer high surface area for H⁺ reduction. It is to be noted that BN/BCN–MoS₂ and G/BCN–MoS₂ (1:2) nanocomposites show surface areas of 540 m² g⁻¹ and 512 m² g⁻¹, respectively, while the physical mixture of the same overall composition exhibits a lower surface area of 208 m² g⁻¹.

C₃N₄–NRGO and C₃N₄–MoS₂ nanocomposites: Covalently linked C₃N₄–NRGO and C₃N₄–MoS₂ composites were examined for HER in an aqueous solution containing TEOA as a sacrificial agent under UV–vis light. Under UV-Vis light illumination, C₃N₄ alone exhibits an activity of 52 μmol h⁻¹ g⁻¹ with a TOF of 0.005 h⁻¹, whereas chemically bonded C₃N₄–NRGO shows an improved activity of 323 μmol h⁻¹ g⁻¹ with a TOF of 0.06 h⁻¹ [Fig. 1(c)].¹⁹

The physical mixture of C₃N₄ and NRGO shows an activity of only 32 μmol h⁻¹ g⁻¹ with a TOF of 0.006 h⁻¹. Interestingly, the chemically bonded C₃N₄–MoS₂ nanocomposite exhibits an extraordinarily high activity of 12 778 μmol h⁻¹ g⁻¹ with a TOF of 2.35 h⁻¹, while that of the physical mixture of C₃N₄ and MoS₂ is only 187 μmol h⁻¹ g⁻¹ with a TOF of 0.04 h⁻¹, as presented in Fig. 1(d). These results demonstrate the benefit of covalent cross-linking for superior HER activity. The superior HER activity of covalently linked nanocomposites is attributed to the enhanced charge-transfer rate as well as greater planarity of the cross-linked layers.

TABLE IV. Comparison of HER activity of covalently linked nanocomposites with some of the literature reports.

<table>
<thead>
<tr>
<th>Photocatalyst system</th>
<th>Reaction conditions</th>
<th>Activity (μmol h⁻¹ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eosin Y (EY)/1T-MoS₂</td>
<td>TEOA; 300 W xenon lamp</td>
<td>30 000</td>
</tr>
<tr>
<td>EY/2H-MoS₂</td>
<td>TEOA; 100 W halogen lamp</td>
<td>70</td>
</tr>
<tr>
<td>EY/MoS₂–IBz</td>
<td>TEOA; 100 W halogen lamp</td>
<td>68</td>
</tr>
<tr>
<td>EY/MoS₂–CH₂COOH</td>
<td>TEOA; 100 W halogen lamp</td>
<td>1 663</td>
</tr>
<tr>
<td>C₃N₄</td>
<td>TEOA; 100 W halogen lamp</td>
<td>52</td>
</tr>
<tr>
<td>EY/BCN</td>
<td>TEOA; 100 W halogen lamp</td>
<td>136</td>
</tr>
<tr>
<td>EY/phosphorene</td>
<td>TEOA; 100 W halogen lamp</td>
<td>960</td>
</tr>
<tr>
<td>EY/MoS₂–MoS₂</td>
<td>TEOA; 100 W halogen lamp</td>
<td>1 752</td>
</tr>
<tr>
<td>EY/MoS₂–RGO (3:1)</td>
<td>TEOA; 100 W halogen lamp</td>
<td>1 384</td>
</tr>
<tr>
<td>EY/MoS₂–RGO (2:1)</td>
<td>TEOA; 100 W halogen lamp</td>
<td>1 307</td>
</tr>
<tr>
<td>MoS₂–C₃N₄</td>
<td>TEOA; 100 W halogen lamp</td>
<td>12 778</td>
</tr>
<tr>
<td>EY/MoS₂–NRGO</td>
<td>TEOA; 100 W halogen lamp</td>
<td>323</td>
</tr>
<tr>
<td>G/BCN–MoS₂</td>
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<td>6 977</td>
</tr>
<tr>
<td>BN/BCN–MoS₂</td>
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<td>C₃N₄–MoS₂</td>
<td>TEOA; 300 W Xe lamp</td>
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<tr>
<td>Black phosphorous–C₃N₄</td>
<td>Methanol; 320 W Xe lamp</td>
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</tr>
<tr>
<td>EY/black phosphorous–MoS₂</td>
<td>Na₂S/Na₂SO₃; 300 W Xe lamp</td>
<td>1 286</td>
</tr>
</tbody>
</table>

*aCovalently linked nanocomposites solely reported in the present study.
*bNanocomposites obtained by Sonogashira coupling.
*cNanocomposites obtained by EDC coupling.
In order to account for the photoexcited electron-transfer in these composites, we obtained the relative band positions of the individual components from control experiments, photoluminescence (PL) studies, as well as density functional theory (DFT) calculations. In the control experiments, HER activities of C$_2$N$_4$, MoS$_2$, and NRGO were recorded in the presence of TEOA. C$_2$N$_4$ alone yielded 52 $\mu$mol h$^{-1}$ g$^{-1}$ while NRGO and MoS$_2$ were inactive. PL studies indicate that the C$_2$N$_4$ signal at 440 nm is drastically quenched in the case of C$_2$N$_4$–NRGO and C$_2$N$_4$–MoS$_2$ composites due to charge-transfer from photoexcited C$_2$N$_4$ to NRGO or MoS$_2$. Electron-transfer from C$_2$N$_4$ to MoS$_2$ (NRGO) is possible only when the conduction band minimum (CBM) of C$_2$N$_4$ is higher in energy than that of MoS$_2$ (NRGO). On photo-excitation, electrons from the valence band maximum (VBM) of C$_2$N$_4$ are excited to CBM and then transferred to CBM of NRGO or MoS$_2$ where reduction of H$^+$ takes place. DFT calculations also suggest that charge-transfer in the covalently linked composites occurs simultaneously through space and bonds between the cross-linked layers. The lack of directional bonds in the physical mixture reduces the homogeneity of the heterolayers and the magnitude of charge-transfer between the layers.

Phosphorene covalently linked with C$_2$N$_4$ and BCN: P–C$_2$N$_4$ and P–BCN nanocomposites, reported for the first time in the present study: The P–C$_2$N$_4$ nanocomposites were examined for the photocatalytic HER in an aqueous solution of TEOA as the sacrificial agent under visible light illumination, while the photocatalytic HER of P–BCN nanocomposites was studied under a similar condition in the presence of the photosensitizer (EY dye). The yields of H$_2$ evolved by P–BCN and P–C$_2$N$_4$ nanocomposites are compared in Fig. 2(a) with the activities of parent phosphorene, BCN, and C$_2$N$_4$ alone. Phosphorene alone shows an activity of 960 $\mu$mol g$^{-1}$ h$^{-1}$, whereas the cross-linked P–BCN and P–C$_2$N$_4$ exhibit a high activity of 6528 $\mu$mol g$^{-1}$ h$^{-1}$ and 11 274 $\mu$mol g$^{-1}$ h$^{-1}$, respectively. The improved activity in the case of P–BCN and P–C$_2$N$_4$ is attributed to the increased surface area as well as to the enhanced charge-transfer rate between the cross-linked components. The activity is higher in the case of P–C$_2$N$_4$ compared to P–BCN possibly due to the correct band positions of bonded phosphorene for efficient charge-transfer from C$_2$N$_4$. The cycling study of the P–C$_2$N$_4$ photocatalysts shows HER activity to be robust [Fig. 2(b)]. In addition, we have found extraordinary photocatalytic activity in the case of P–MoS$_2$ nanocomposites and these results are discussed in Sec. V.

Table IV presents the HER activity of various abovementioned covalently linked nanocomposites along with some of the literature reports.

G/BCN–MoS$_2$ and BN/BCN–MoS$_2$ nanocomposites for electrochemical HER: Encouraged by the superior photocatalytic activity of G/BCN–MoS$_2$ and BN/BCN–MoS$_2$, we have examined them for electrochemical HER using a conventional three-electrode cell with H$_2$SO$_4$ as the electrolyte. Linear sweep voltammetry (LSV) curves of the BN/BCN–MoS$_2$ and G/BCN–MoS$_2$ nanocomposites along with that of the physical mixtures are presented in Fig. 3(a), where data on a commercial platinum catalyst (Pt/C, 40 wt. %) are also included for estimation. The BN/BCN–MoS$_2$ and G/BCN–MoS$_2$ catalysts show a positive shift in the onset potential ($\eta$) compared to the individual constituents as well as the physical mixture. The BN/BCN–MoS$_2$ (1:2) and G/BCN–MoS$_2$ (1:2) nanocomposites exhibit positive shifts of 30 mV and 45 mV in $\eta$ ($\approx$ 0.05 V and $\approx$ 0.035 V) as compared to the BCN and MoS$_2$ physical mixture which shows an $\eta$ value of $\approx$ 0.063 V, confirming their superior HER activity. To gain insight into the kinetics of H$_2$ evolution on the BN–MoS$_2$ nanocomposites, Tafel slopes were evaluated [Fig. 3(b)], BN/BCN–MoS$_2$ and G/BCN–MoS$_2$ (1:2) show Tafel slopes of 36 mV dec$^{-1}$ and 33 mV dec$^{-1}$, respectively, comparable to that of Pt/C (29 mV dec$^{-1}$), which suggests the efficacy of covalently bonded layers in fast electron transport by the Volmer–Tafel mechanism.

V. EFFECTS OF THE RELATIVE PROPORTION OF THE 2D LAYERS AND THE LINKER ON HER ACTIVITY (EG–MoS$_2$ NANOCOMPOSITES REPORTED FOR THE FIRST TIME IN THE PRESENT STUDY)

We had discussed the HER activity of MoS$_2$–RGO nanocomposites of different compositions prepared by Sonogashira coupling in Sec. IV. In order to further examine the effect of relative proportions of different 2D layers on the HER, we have investigated EG–MoS$_2$ composites with different MoS$_2$ and exfoliated graphene (EG) contents, 2:1, 1:1, and 1:2, by EDC coupling (see the supplementary material for more details). The hydrogen evolution experiments were carried in aqueous solutions of TEOA under visible light in the presence of the EY dye as a photosensitizer. The EG–MoS$_2$ (1:2) composite with a high MoS$_2$ content shows a higher activity of 367 $\mu$mol g$^{-1}$ h$^{-1}$, whereas EG–MoS$_2$ (1:1) and (2:1) show an activity of only 305 $\mu$mol g$^{-1}$ h$^{-1}$ and 184 $\mu$mol g$^{-1}$ h$^{-1}$, respectively [Fig. 4(a)]. Under similar conditions, ethylene amine functionalized MoS$_2$ (MoS$_2$–CH$_2$NH$_2$) alone shows an activity of 98 $\mu$mol g$^{-1}$ h$^{-1}$, while acid functionalized EG (EG–COOH) does not exhibit any notable H$_2$ evolution. The above results suggest that MoS$_2$ is the active component for hydrogen evolution in these.
nanocomposites and the activity decreases with the increase in the graphene content. We have examined the role of the proportion of the linker between the covalently linked EG–MoS$_2$ layers on the HER activity. For this purpose, we have prepared amine containing MoS$_2$ (MoS$_2$–CH$_2$–CH$_2$–NH$_2$) with two different amounts of functionalization independently, 11 wt.% and 20 wt.% [as determined from thermogravimetric analysis (TGA)], and cross-linked them with acid functionalized EG (see the supplementary material for more details). Thermogravimetric analysis curves of MoS$_2$–CH$_2$–CH$_2$–NH$_2$ with different amounts of functionalizations [Fig. S1(a)] show a weight loss of 11 wt.% and 20 wt.% due to decomposition of organic groups bonded to MoS$_2$ units. The EG–MoS$_2$ (1:2, 20 wt.%) composite with a higher proportion of the linker between the cross-linked layers shows ∼9× higher activity than the EG–MoS$_2$ (1:2, 11 wt.%) composite [Fig. 4(b)]. This implies that an increase in the proportion of the linkers between the cross-linked components enhances the activity, possibly by increasing charge-transfer rates along with the increased interfacial area between the cross-linked components.

2D MoS$_2$ is known to be active for photo/electrocatalytic HER. Phosphorene possesses a lone pair of electrons on the phosphorus atom which can interact with MoS$_2$ and play a role in giving rise to higher activity in P–MoS$_2$ composites. We, therefore, considered it worthwhile to investigate the HER performance of phosphorene covalently linked to MoS$_2$. We have investigated phosphorene–MoS$_2$ nanocomposites with different phosphorene and MoS$_2$ contents, 2:1, 1:1, and 1:2, prepared by EDC coupling. P–MoS$_2$ (1:1) and (1:2) composites show a comparable activity of 25 734 μmol g$^{-1}$ h$^{-1}$ and 24 628 μmol g$^{-1}$ h$^{-1}$, respectively, whereas P–MoS$_2$ (2:1) with a high phosphorene content shows a slightly lower activity of 22 943 μmol g$^{-1}$ h$^{-1}$ [Fig. 4(c)]. Unlike MoS$_2$–EG, the proportion of the 2D layers did not alter the catalytic activity greatly since both the cross-linked components are intrinsically active for HER.$^{21}$ On the other hand, we observed enhanced activity in the case of P–MoS$_2$ (1:2, 20 wt.%) with a high proportion of the linker between the cross-linked layers as compared to P–MoS$_2$ (1:2, 11 wt.%) [Fig. 4(d)]. TGA curves of P–MoS$_2$ composites with 20 wt.% and 11 wt.% of the linker are given in Fig. S1(b). The HER activities of MoS$_2$–EG and P–MoS$_2$ composites with different proportions of the 2D layers and the linker are listed in Table V.

VI. EFFECT OF THE INTER-PLANAR SEPARATION ON HER ACTIVITY

In a recent study, we have investigated covalently cross-linked MoS$_2$ layers with MoS$_2$ or with graphene layers using

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**TABLE V.** Comparison of the HER activity of EG–MoS$_2$ and P–MoS$_2$ nanocomposites with different proportions of the 2D layers and the linker.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Activity (μmol h$^{-1}$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EY/EG–MoS$_2$ (2:1)$^a$</td>
<td>184</td>
</tr>
<tr>
<td>EY/EG–MoS$_2$ (1:1)$^a$</td>
<td>307</td>
</tr>
<tr>
<td>EY/EG–MoS$_2$ (1:2, 11 wt. %)$^a$</td>
<td>367</td>
</tr>
<tr>
<td>EY/EG–MoS$_2$ (1:2, 20 wt. %)$^a$</td>
<td>2258</td>
</tr>
<tr>
<td>EY/P–MoS$_2$ (2:1)$^a$</td>
<td>29 396</td>
</tr>
<tr>
<td>EY/P–MoS$_2$ (1:1)</td>
<td>25 734</td>
</tr>
<tr>
<td>EY/P–MoS$_2$ (1:2, 20 wt. %)$^a$</td>
<td>24 628</td>
</tr>
<tr>
<td>EY/P–MoS$_2$ (1:2, 11 wt. %)$^a$</td>
<td>9 568</td>
</tr>
</tbody>
</table>

$^a$Covalently linked nanocomposites solely reported in the present work.
linkers of varying length by the Sonogashira coupling strategy (Scheme S1). Linkers used for cross-linking are 1,4-phenylene, 1,4-diethynylbenzene, and 4,4′-diethynylbiphenyl, and they are named L1, L2, and L3, respectively. Different nanocomposites obtained by cross-linking MoS2 with MoS2 are MoS2–1,4-phenylene–MoS2, MoS2–1,4-diethynylbenzene–MoS2, and MoS2–4,4′-diethynylbiphenyl–MoS2, and they are designated as M–L1–M, M–L2–M, and M–L3–M, respectively. Nanocomposites generated by linking MoS2 layers with graphene are MoS2–1,4-phenylene–graphene, MoS2–1,4-diethynylbenzene–graphene, and MoS2–4,4′-diethynylbiphenyl–graphene, and they are designated as M–L1–G, M–L2–G, and M–L3–G, respectively. Photocatalytic HER activity was performed by the dye-sensitized method using EY as the sensitizer. The HER activity of 3720 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), 365 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), and 255 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), respectively, implies a decrease in activity with the increase in the linker length [Fig. 5(a)]. These results demonstrate the decrease in the charge-transfer rate and hence overall HER activity with the increase in the linker length between the cross-linked MoS2 sheets. DFT calculations have been performed to elucidate the mechanism behind the enhanced photocatalytic HER activity with decreasing inter-layer spacing. These studies suggest that the electron transfer from photoexcited dye to cross-linked MoS2 layers is more efficient in the case of M–L–M and M–L–G composites with a shorter inter-layer spacing. On the other hand, an increase in the inter-layer spacing between the components, with a lengthy linker, causes confinement of charge redistribution close to the interface region, leading to the decreased charge transfer between the MoS2 and other 2D layers and hence overall HER activity. Graphene–MoS2 composites, M–L1–G, M–L2–G, and M–L3–G, exhibit an HER activity of 3720 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), 1138 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), and 391 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), respectively, with the HER activity decreasing with increasing interlayer distance between cross-linked components, similar to MoS2 nanocomposites [Fig. 5(b)]. Higher activity in the case of MoS2–graphene composites is attributed to the enhanced charge-transfer from more conducting graphene to catalytically active MoS2 sites through the 3D network. Clearly, the nature of the 2D sheets, the inter-layer distance, and the nature of the linker all provide pathways to tune the properties of the covalently linked nanocomposites.

VII. CONCLUDING REMARKS

The above discussion should indicate that the covalent cross-linking of layers of 2D materials is a useful strategy to generate novel 2D materials with interesting properties, specially HER activity. Although we have discussed covalent cross-linking at length, it should be noted that the heteroassemblies can also be generated by supramolecular means. Xiong et al. have reported the synthesis of unilamellar graphene/MoS2 superlattices by the solution phase electrostatic assembly between positively charged graphene and negatively charged MoS2. We used this strategy to prepare several nanocomposites including graphene, BCN, and MoS2 and to study their HER activity. There are, however, certain special features of covalent linking of 2D layers. In the van der Waals heterostructures, ladder-like assemblies are not possible. Furthermore, there is no “chemical” interaction between layers, and charge-transfer would be negligible. The same would be true in the structures prepared by the electrostatic interaction of layers. The supramolecular (noncovalent) interaction would also not give rise to interactions responsible for good catalytic activity. We, therefore, feel that covalent linking is unique in giving rise to nanocomposites with good catalytic and other properties.

SUPPLEMENTARY MATERIAL

See the supplementary material for EG–MoS2 and P–MoS2 composite synthesis with varying proportion of the 2D layers and the linker, TGA curves of amine functionalized MoS2 with two different proportions of amine functionalities, TGA curves of the P–MoS2 composite with varying proportion of the linker, and a schematic representation of the assemblies of covalently cross-linked nanosheets of MoS2 with varying linker length.

ACKNOWLEDGMENTS

K.P. thanks SSL for the post-doctoral fellowship. P.V. thanks SSL and DST Nano Mission for the postdoctoral fellowship.

REFERENCES

PERSPECTIVE