Remarkable photochemical HER activity of semiconducting 2H MoSe₂ and MoS₂ covalently linked to layers of 2D structures and of the stable metallic 1T phases prepared solvo- or hydro-thermally[§]

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Abstract. MoS₂ and MoSe₂ in the stable semiconducting 2H form show negligible photocatalytic activity for the hydrogen evolution reaction (HER). By linking the layers of the dichalcogenide with layers of other 2D materials such as carbon-rich borocarbonitride (BC₇N), one can enhance the photochemical HER activity significantly. Interestingly, such nanocomposites, MoSe₂–MoSe₂ and MoSe₂–BCN show high photocatalytic activity even though the dichalcogenide itself is in the 2H form. This study shows the important role played by covalent cross-linking of layered compounds. Photocatalytic activity of covalently cross-linked layer of 2H-MoSe₂ is higher than that of 2H-MoS₂. Unlike the 2H forms, the metallic 1T forms of MoS₂ and MoSe₂ prepared by lithium intercalation followed by exfoliation, exhibit high photocatalytic HER activity. Unfortunately, materials prepared by lithium intercalation are unstable. The 1T forms of MoSe₂ and MoS₂ prepared by solvothermal or hydrothermal methods are, however, quite stable and exhibit good photochemical activity for HER. The 1T forms are generally superior to the covalently linked 2H forms. The present study shows how MoSe₂ and MoS₂ in both 2H and 1T forms can be exploited for photochemical HER activity by appropriate chemical manipulation.

Keywords. Photochemical hydrogen evolution; Covalent cross-linking; Borocarbonitrides; Mo dichalcogenides; 1T-MoSe₂; 1T-MoS₂; EDC coupling.

1. Introduction

Of the variety of materials being investigated for water splitting to generate hydrogen,^{1–4} MoS₂ has gained considerable importance. Thus, unlike the semiconducting 2H form of MoS₂, the metallic 1T form exhibits outstanding performance in photochemical hydrogen generation, the 1T form of MoSe₂ being even better. These 1T forms are obtained in the form of nanosheets by intercalating lithium in the stable 2H-MoS₂ or MoSe₂ followed by exfoliation in water. 1T-MoS₂ and MoSe₂ prepared in this way are unstable, and transform to the stable 2H forms on keeping.⁵ Stable 1T-MoS₂ and

MoSe₂ have, however, been prepared by hydrothermal and solvothermal methods.⁶ An interesting discovery in recent months is the advantage of coupling sheets of stable 2H-MoS₂ with other layered materials to enhance the catalytic activity for hydrogen evolution (HER).^{7–10} One of the important members of this class of materials obtained by cross-linking two layered structures is that obtained by cross-linking MoS₂ with a carbon-rich borocarbonitride, BC₇N.⁹ Note that MoS₂ here is in 2H form. Since it is known that MoSe₂ may have more desirable characteristics for use as a catalyst for hydrogen generation,⁵ we considered it important to investigate HER activity of MoSe₂ cross-linked with the other 2D materi-

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[§] Dedicated to Prof. M V George on the occasion of his 90th birthday.

als. We should recall that 1T-MoSe₂ sheets are superior to sheets of 1T-MoS₂ as catalysts in the photochemical generation of hydrogen.⁵ In view of this background, we have investigated nanosheets of 2H-MoSe₂ cross-linked with C₃N₄ and the carbon-rich borocarbonitride, BC₇N. We have used the simpler term BCN, to designate this material. We have designated the BCN-MoSe₂ composites where BN domains of borocarbonitride are cross-linked to MoSe₂ nanosheets as BN/BCN-MoSe₂ and the composites where the graphene domains of borocarbonitride are cross-linked with MoSe₂ sheets as G/BCN-MoSe₂. In addition, we have investigated assemblies of MoSe₂ layers in order to compare the performance of these materials with those of single layer of MoSe₂ and cross-linked layers of MoS₂.

Besides investigating the photochemical generation of hydrogen with semiconducting 2H-MoSe₂^{11,12} covalently bonded with sheets of C₃N₄,^{13,14} BC₇N^{15,16} and with itself, we have examined photochemical hydrogen generation by the metallic 1T forms of MoS₂ and MoSe₂ prepared by hydrothermal and solvothermal methods. It is to be noted that the 1T forms of Mo dichalcogenides^{17,18} prepared solvothermally or hydrothermally would not be expected to be identical to the 1T forms prepared by Li-intercalation and exfoliation, differing in surface properties.

2. Experimental

2.1 Synthesis of cross-linked MoSe₂ nanosheets

MoSe₂ layers cross-linked with the layers of other 2D materials were generally prepared as follows. Nanosheets of 1T-MoSe₂ were generated by lithium intercalation of 2H-MoSe₂, followed by exfoliation in deionized water.⁵ 1T-MoSe₂ layers were reacted with a 10-fold excess of 2-bromoacetic acid to obtain the surface carboxyl groups by

forming the C-Se bond (MoSe₂-CH₂COOH). The surface carboxyl groups of MoSe₂ were utilized to link with nanosheets of other 2D materials. Similarly, 1T-MoSe₂ layers were reacted with a 12-fold excess of the 4-iodoaniline to obtain the surface amine groups by forming the C-Se bonds¹⁹ (MoSe₂-C₆H₄NH₂). The surface amine groups of MoSe₂ were utilized for linking with other sheets.

Assemblies of MoSe₂ could be prepared by the reaction of 1T-MoSe₂ with diazonium salt of 4-iodoaniline to obtain iodobenzene functionalized MoSe₂ (MoSe₂-C₆H₄I), followed by addition of 1T-MoSe₂ to form MoSe₂ assemblies by forming the C-Se bonds¹⁹ (MoSe₂-C₆H₄-MoSe₂) (Scheme 1).

To obtain cross-linked MoSe₂-C₃N₄, MoSe₂-CH₂COOH (30 mg) and C₃N₄ (30 mg) were dispersed in dry DMF in N₂ atmosphere. To the above dispersion, equal amounts of 1-hydroxybenzotriazole (HOBt, 30 mg) and N-(3-(dimethylamino)propyl)-N'-ethylcarbodiimidehydrochloride (EDC·HCl, 30 mg) were added along with N,N-diisopropyl ethylamine (DIPEA, 500 μL) and stirred at room temperature for 48 h in an inert atmosphere which was maintained during the reaction. The solid product was collected by filtering, then washed with DMF and dried at 60 °C under vacuum (Scheme 2).

Borocarbonitride nanosheets were synthesized by using a protocol reported elsewhere.^{15,20} Starting with activated charcoal (500 mg), urea (2.4 g) and boric acid (60 mg) were heated in a furnace at 900 °C in N₂ atmosphere for 10 h. The black product was treated with NH₃ at 900 °C for 5 h. Hence, these are the two possible ways of linking MoSe₂ nanosheets of other 2D materials: by linking to BN domains in BC₇N (BN/BCN-MoSe₂) and by linking to graphene (G) domains in BC₇N (G/BCN-MoSe₂) as shown in Scheme 3.

2.2 Solvothermal synthesis of 1T-MoS₂ and 1T-MoSe₂

1 mmol of MoCl₅ (from Alfa Aesar, 99% Purity) and 10.1 mmol of thioacetamide (CH₃CSNH₂) (Loba Chemie, 99% Purity) were dissolved in 30 mL of DMF (SD Fine chemicals, 99% Purity). The solution was stirred for 30 min and then

Scheme 1. Synthetic strategy for covalently cross-linked MoSe₂-MoSe₂ nanocomposites.

Scheme 2. Synthetic strategy for covalently cross-linked $\text{MoSe}_2\text{-C}_3\text{N}_4$ nanocomposites.

transferred to a 25 mL Teflon-lined autoclave. The autoclave was heated at 200°C for 30 h.²¹ Similarly, $1T\text{-MoSe}_2$ was prepared in DMF taking 0.1 mmol of MoCl_5 , and 3 mmol of selenourea (Alfa Aesar, 99% Purity) dissolved in 20 mL of DMF. The solution was stirred for 30 min and transferred to a 25 mL Teflon-lined autoclave. The autoclave was heated up to 200°C for 48 h. Then autoclave was allowed to cool to room temperature, and the product was washed several times with water and ethanol and dried at 60°C under vacuum.

2.3 Hydrothermal synthesis of $1T\text{-MoS}_2$ and $1T\text{-MoSe}_2$

$1T\text{-MoS}_2$ was synthesized hydrothermally by dissolving 1 mmol of $(\text{NaMoO}_4 \cdot 2\text{H}_2\text{O})$ (Merck 99%) and 3 mmol of thiourea ($\text{CS}(\text{NH}_2)_2$, SD Fine chemicals, 99%) in a solution of water and propionic acid (2:1). The solution was magnetically stirred for 30 min then transferred into 25 mL Teflon-lined autoclave, heated at 200°C for 4 h.²² Selenourea was used as a precursor to synthesize $1T\text{-MoSe}_2$. $1T\text{-MoSe}_2$ was synthesized by dissolving 1 mmol of $(\text{NaMoO}_4 \cdot 2\text{H}_2\text{O})$ (Merck 99%) and 3 mmol of selenourea (Alfa Aesar chemicals, 99%) in a solution of water and propionic acid (2:1). The solution was stirred for 30 min and then transferred into a 25 mL Teflon-lined autoclave, heated at 200°C for 4 h. The autoclave was allowed to cool to room temperature and the product washed several times with water and alcohol and allowed to dry at 60°C in a vacuum oven for 24 h.

2.4 Characterization

Fourier-transform infrared (FTIR) spectra were recorded with Bruker IFS 66v/S spectrometer. Scanning electron microscope (SEM) images were obtained with FEI Nova Nano SEM 600 microscope. Powder X-ray diffraction (PXRD) data were collected with Bruker diffractometer ($\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) X-ray source). Raman spectra were collected with Jobin Yvon LabRam HR spectrometer using Ar-laser ($\lambda = 514.5 \text{ nm}$). Transmission electron microscope (TEM) images were collected by FEI Tecnai microscope,

operating at 200 kV accelerating voltage. High-resolution TEM (HRTEM) was obtained with FEI Titan aberration-corrected electron microscopy. X-ray photoelectron spectra (XPS) was recorded with an Omicron spectrometer using $\text{Al K}\alpha$ as the X-ray source (1486.6 eV). N_2 adsorption-desorption isotherms (77 K) were obtained using a QUANTACHROME QUADRASORB-SI analyzer. The samples were first heated in vacuum at 80°C for approximately 24 h and then the adsorbate charged into the sample tube. The pressure change was monitored to observed a decrease in pressure at equilibrium, using which the degree of adsorption was determined.

2.5 Photocatalytic hydrogen evolution reaction

Scheme 4 shows the principle of the method we have used. 2.5 mg of the catalyst was dispersed in an aqueous solution of triethanolamine (15% v/v, 48 mL) by sonication in a cylindrical glass vessel. Eosin Y (14 μmol) was added as a sensitizer. This mixture was illuminated with a halogen lamp (100 W) under constant stirring. The evolved gas was manually collected from the headspace and analyzed with a gas chromatograph equipped with a thermal conductivity detector (PerkinElmer ARNL 580C).

The model in Scheme 4 represents a singlet ground-state as EY, excited singlet state EY^{1*} , and low lying triplet state EY^{3*} . The highly reducing negatively charged state (EY^-) forms in the presence of triethanolamine (TEOA). The electron from the reducing species is transferred to the catalyst for hydrogen evolution reaction.

3. Results and Discussion

We have synthesized the covalent composite of MoSe_2 by cross-linking with other 2D materials such as C_3N_4 , BC_7N and with itself. MoSe_2 cross-linked to C_3N_4 and BC_7N and as well as the assembly of MoSe_2 were characterized by FTIR and Raman spectroscopy, X-ray diffraction and other techniques.

Scheme 3. Synthetic strategy for covalently cross-linked G/BCN-MoSe₂ and BN/BCN-MoSe₂ nanocomposites (EDC = 1-ethyl-3-(3 dimethylaminopropyl)carbodiimide).

Scheme 4. Simplified electronic state diagram of Eosin Y and plausible mechanism of H₂ reaction.

The Fourier-transform infrared (FTIR) spectrum of MoSe₂-CH₂COOH shows strong bands at 1758 and 3210 cm⁻¹ which correspond to C=O and -OH stretching vibrations of carboxylic groups beside with a C-Se stretching band at 736 cm⁻¹ arising from covalent functionalization. BC₇N displays a strong band at 1591 cm⁻¹ and a weak band around 1723 cm⁻¹ arising from C=C and C=O stretching vibrations respectively.

Figure 1. (a, b) Infrared spectra of MoSe₂ and its nanocomposites.

along with a broad band in the 3065–3485 cm⁻¹ region corresponding to the residual amine and hydroxyl groups. The broad band around 950–1250 cm⁻¹ is due to C–O stretching and O–H bending vibrations. The C=O stretching band in G/BCN–MoSe₂ composite at 1638 cm⁻¹ along with other characteristic bands from amino benzene moieties suggests the formation of amide linkages between carboxylic groups of graphene domains of BC₇N and amine functionalized MoSe₂. Similarly, BN/BCN–MoSe₂ nanocomposite shows a carbonyl stretching band at 1676 cm⁻¹, confirming cross-linking of the BC₇N and MoSe₂ layers by the amide bond (Figure 1a and b).²³

Raman spectroscopy plays a crucial role in determining the stable form of MoSe₂ structure in the cross-linked nanocomposite. We show typical Raman spectra of BCN–MoSe₂ nanocomposite are presented in Figure 2. The spectra of the G/BCN–MoSe₂ and BN/BCN–MoSe₂ nanocomposites show characteristic D and G bands of BC₇N at 1349 and 1606 cm⁻¹, respectively, along with the A_{1g} and E_{2g} bands of MoSe₂ at 244

and 291 cm⁻¹, respectively.²⁴ MoSe₂ in the cross-linked nanocomposite is observed to be in 2H form.

The formation of covalent cross-linked assemblies was also investigated using powder X-ray diffraction (PXRD) patterns of BN/BCN–MoSe₂, G/BCN–MoSe₂ and MoSe₂–C₃N₄ nanocomposites which showed the appearance of new reflections at $2\theta = 13.19^\circ$ ($d = 0.67$ nm), 12.76° ($d = 0.69$ nm) and 13.09° ($d = 0.68$ nm) corresponding to the interlayer spacing between BC₇N–MoSe₂ and MoSe₂–C₃N₄ nanocomposites (Figure S1, Supplementary Information). Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of the MoSe₂ assemblies, G/BC₇N–MoSe₂ and BN/BC₇N–MoSe₂ showed evidence for layer-by-layer assembly of sheet structure upon cross-linking of the constituent MoSe₂ and BC₇N layers (Figure 3a to f).

Values of surface area obtained from BET N₂ adsorption-desorption isotherms (at 77 K) for BC₇N–MoSe₂, MoSe₂–MoSe₂, MoSe₂–C₃N₄ nanocomposites and MoSe₂ done are 580, 312, 280 and 78 m²/g respectively (Figure S4, Supplementary Information). We observe type-I characteristics in the low-pressure region along with a type-II hysteresis loop in the high-pressure region, as per the IUPAC nomenclature.²⁵

The photochemical hydrogen evolution was studied in the presence of Eosin Y (as a sensitizer) in aqueous solution triethanolamine (TEOA, sacrificial agent). The mechanism of hydrogen evolution with Eosin Y and the triethanolamine is well-studied in the literature (Scheme 4).^{5,26} We compare the results of photochemical hydrogen yields of nanocomposites of MoS₂ and MoSe₂. Pristine MoS₂ and MoSe₂ show a similar activity of 1663 and 1680 μmol g⁻¹h⁻¹, respectively.⁹

Pristine BC₇N and pristine C₃N₄ show very low activity 165 and 113 μmol g⁻¹h⁻¹, respectively (Figures 4 and S5 (Supplementary Information)). The

Figure 2. Raman spectra of MoSe₂ and its nanocomposites.

Figure 3. (a, b) HRTEM image of MoSe₂ and cross-linked MoSe₂-MoSe₂, (c, d) TEM image of BCN with cross-linking of MoSe₂, BN/BCN-MoSe₂ and G/BCN-MoSe₂, (e, f) SEM image of cross-linked MoSe₂-MoSe₂ and MoSe₂-C₃N₄.

Figure 4. (a, b) Comparison of the H₂ evolution activity of MoSe₂ and its nanocomposites.

self-assembly of MoSe₂, however, shows high activity reaching 8294 μmol g⁻¹h⁻¹. This is much higher than that of MoS₂ assemblies (1750 μmol g⁻¹h⁻¹) synthesized by the same method.⁷

MoSe₂-C₃N₄ nanocomposite exhibits a somewhat lower activity 2624 μmol g⁻¹h⁻¹ compared to MoS₂-C₃N₄. This is unlike BC₇N-MoSe₂ which exhibits a high activity 10384 or 12584 μmol g⁻¹h⁻¹ compared to BC₇N-MoS₂(6965 μmol g⁻¹h⁻¹) (Figures 4 and S5 (Supplementary Information)).⁸⁻¹⁰ It is noteworthy that the photochemical activity and surface area vary in the same fashion. The increased HER activity in the cross-linked composites increases with the surface area as

cross-linking opens up pores and slits where edges can act as HER sites. Moreover, cross-linking increases the planarity of the layer with increased overlap between the cross-linked layers, facilitating charge transfer across the network.⁸ Furthermore, HER with the physical mixture of BCN and MoSe₂ shows very small activity (878 μmol g⁻¹h⁻¹) which is much lower compared to the cross-linked material. This observation suggests that cross-linking has a role in enhancing the HER activity (Table 1).

The activity of assemblies of BCN-MoSe₂ nanocomposite is especially noteworthy. We can compare the performance of the MoSe₂ nanocomposites

Table 1. Photochemical HER activity of nanocomposites of 2H-MoSe₂ cross-linked with other 2D layers

Materials	Surface area (m ² /g)	Activity [$\mu\text{mol g}^{-1}\text{h}^{-1}$]
2H-MoSe ₂	78	1680
BCN	810	165
C ₃ N ₄	29	113
MoSe ₂ -MoSe ₂	312	8294
MoSe ₂ -C ₃ N ₄	280	2624
BN/BCN-MoSe ₂	580	10384
G/BCN-MoSe ₂	576	12584
BCN-MoSe ₂	—	878
Physical mixture		

with those of MoS₂. The performance of MoSe₂ nanocomposites is generally higher than those of MoS₂ nanocomposites, the only exception being the nanocomposite with C₃N₄. Clearly, we can significantly improve the photochemical HER activity of 2H-MoS₂ and 2H-MoSe₂ by covalent cross-linking with other 2D materials.^{7–10}

We were able to synthesize stable 1T-form of bulk MoS₂ and MoSe₂ by solvothermal and hydrothermal routes. The synthetic procedure has been described in the experimental section. The as-synthesized samples were characterized by Raman spectroscopy. The Raman spectrum of 1T-MoS₂ synthesized *via* a solvothermal (DMF) route is shown in Figure 5a. The characteristic J₁, J₂ and J₃ bands of 1T-MoS₂ are at 147, 236 and 336 cm⁻¹ respectively. The A_{1g} band characteristic of the 2H-phase has a very low intensity (Figure 5a) suggesting that the sample consists predominantly of the 1T phase. The intensity of the A_{1g} peak increases over long periods indicating slow conversion from 1T to 2H-phase (Figures 5a and S6 (Supplementary Information)). The Raman spectrum of 1T-MoSe₂

exhibits the characteristic J₁, J₂ and J₃ bands appear at 118, 154 and 221 cm⁻¹, respectively. The 1T-phase of MoSe₂ is stable for 2 weeks with no significant change in the relative Raman band intensities (Figure 5b). There was no appearance of the A_{1g} band of the 2H-form during this period. The 1T-phases of MoS₂ and MoSe₂ obtained *via* hydrothermal means also show the characteristic Raman bands. Thus, 1T-MoS₂ exhibits J₁, J₂, J₃ bands at 154, 244 and 340 cm⁻¹ and the intensity of the A_{1g} band due to the 2H phase is insignificant. After 2 weeks, we observed no change in the relative intensities of the bands indicating stability of the 1T-phase (Figure 6a). The Raman spectrum of the 1T-phase of MoSe₂ prepared hydrothermally shows the J₁, J₂ and J₃ bands at 118, 154 and 222 cm⁻¹, respectively. Similar to MoSe₂ synthesized *via* solvothermal route, we see no A_{1g} band due to the 2H phase (Figure 6b). The relative peak intensities of the 1T phase do not change over a period of one week. Figure S7 (Supplementary Information) shows a typical HRTEM image of the 1T-phase obtained *via* the hydrothermal or the solvothermal route.

We have studied the HER activity of both 1T-MoS₂ and 1T-MoSe₂ synthesized by solvothermal and hydrothermal routes in the presence of Eosin Y dye in aqueous solution triethanolamine (15% v/v). The activity of 1T-MoS₂ and 1T-MoSe₂ synthesized in DMF had an activity of 31700 and 57500 $\mu\text{mol g}^{-1}\text{h}^{-1}$ (Figure 7a), the activity of MoSe₂ being considerably higher. Due to similar hydrogen binding energy of Mo and Se, both atoms can act as a hydrogen evolution site in contrast to MoS₂ where only Mo atoms are the HER site.⁵ The activity of the 1T-MoS₂ was studied over a period of 6 weeks.

We observe an activity of 31700, 37700, 37000 and 28000 $\mu\text{mol g}^{-1}\text{h}^{-1}$ for 0, 2, 4 and 6 weeks, respectively (Figure 7b and Table S1 (Supplementary Information)). We observe a decrease in the activity of the samples after

Figure 5. Raman Spectra of (a) 1T-MoS₂ and; (b) 1T-MoSe₂ synthesized solvothermally recorded after different periods to demonstrate the stability of the 1T-phase.

Figure 6. Raman Spectra of (a) 1T-MoS₂ and; (b) 1T-MoSe₂ synthesized hydrothermally recorded after different periods to demonstrate the stability of the 1T-phase.

Figure 7. Comparison of Hydrogen evolution activity of (a) 1T-MoS₂ and 1T-MoSe₂ synthesized solvothermally; (b) and over a period of 6 weeks in the case of MoS₂.

Figure 8. Comparison of hydrogen evolution activity of (a) 1T-MoS₂ and 1T-MoSe₂, synthesized using a hydrothermal route; (b) and over a period of 2 weeks in the case of 1T-MoS₂.

6 weeks due to slow conversion of the 1T to the 2H-phase as observed from Raman spectra (Figure S6, Supplementary Information). Stable HER evolution over long periods is observed from cycling studies (Figure S8, Supplementary Information).

HER activity of the 1T-phases of MoS₂ and MoSe₂ synthesized *via* hydrothermal means was 17000 and 35000 $\mu\text{mol g}^{-1}\text{h}^{-1}$, respectively (Figure 8a). Similar to the 1T-samples synthesized in DMF, we observe higher activity in the case of MoSe₂. The activity of 1T-MoS₂

Table 2. Comparison of photochemical hydrogen evolution by the 1T-phases of MoS₂ and MoSe₂ synthesized by different methods.

	Synthetic method	Activity [$\mu\text{moles g}^{-1}\text{h}^{-1}$]	TOF [h^{-1}]
1T- MoS ₂	(a) Li-intercalation and exfoliation ⁵	30,000	4.8
	(b) MoCl ₅ + Thioacetamide in DMF, 200 °C (Solvothermal)	37,000	6.0
	(c) Na ₂ MoO ₄ · 2H ₂ O + Thiourea in water + propionic acid, 200 °C (Hydrothermal)	16,000	2.5
1T- MoSe ₂	(a) Li-intercalation and exfoliation ⁵	75,000	19.0
	(a) MoCl ₅ + Selenourea in DMF, 200 °C (Solvothermal)	57,500	14.6
	(c) Na ₂ MoO ₄ · 2H ₂ O + Selenourea in water + propionic acid, 200 °C (Hydrothermal)	35,000	8.9

was studied for two weeks. The activity after 2 weeks was 14000 $\mu\text{mol g}^{-1}\text{h}^{-1}$ (Figure 8b and Table S2 (Supplementary Information)).

We have compared the photochemical activity of the 1T phase obtained by solvothermal and hydrothermal methods with that synthesized from Li-intercalation and exfoliation in Table 2. The 1T phase from solvothermal and hydrothermal methods show comparable photocatalytic activities and are suitable for practical use. In this aspect, 1T phases are superior to the nanocomposites obtained by covalent linking of layer structures.

4. Conclusions

The present study shows that it is possible to utilize the semiconducting 2H phases of MoS₂ and MoSe₂ as photocatalysts for HER by forming covalently linked nanocomposites with other 2D materials such as BC₇N or by self-assembly. The photochemical activity of covalently cross-linked nanocomposites is sufficiently high for possible practical use (though not as high as that of the 1T phases). The performance of MoS₂ and MoSe₂ nanocomposites with a borocarbonitride such as BC₇N is noteworthy. It is interesting that by linking MoS₂ and MoSe₂ to another 2D material one can enhance the photochemical activity substantially. Cross-linking of 2H-MoS₂ and MoSe₂ with BC₇N and C₃N₄ is likely to involve charge transfer between the two heterolayers.

It is gratifying that stable 1T-MoS₂ and MoSe₂ can be synthesized by simple hydrothermal and solvothermal methods. The 1T samples so prepared are stable (upto 2–4 weeks) unlike those obtained by lithium intercalation followed by exfoliation. Photochemical HER activity of 1T MoS₂ and 1T MoSe₂ is remarkable and can be of practical use.

Supplementary Information (SI)

Detailed information about nanocatalysts characterization techniques, XPS of BC₇N (Figure S2), XPS of iodobenzene functionalized MoSe₂ and cross-linked MoSe₂ (Figure S3) are provided in the supplementary information. Supplementary information is available at www.ias.ac.in/chemsci.

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