Eng. Sci., 2022, **20**, 34–46

Engineered Science

DOI: https://dx.doi.org/10.30919/es8d755

Physical Modifications and Algorithmic Predictions behind Further Advancing Two-dimensional Water Splitting Photocatalyst: An Overview

Indrajit Chakraborty,[1] Zhanhu Guo,[2] Anirban Bandyopadhyay[3] and Pathik Sahoo[3, 4, 5*]

Abstract

It is becoming increasingly important to consider physical dimensions in addition to chemical capabilities when designing material for a specific feature. The physical dimensions, optical properties, surface area, and mechanical properties of material all play a role in determining its photochemical capabilities. In the two-dimensional (2D) materials, the surface area for the photoelectric effect and the long-range conductivity for homogeneous charge distribution in the photochemical reactions are perfectly balanced. A wide range of 2D materials has been investigated to date: low-cost, stable, earth-abundant, and hazard-free. However, photocatalyst efficiency must be improved to meet modern society's growing green energy demand. Photocatalysts are particularly interested in storing solar energy in chemical bonds to provide long-term energy. Researchers from various fields have recently contributed to properly arranging photocatalytic reaction centers in space, tuning the bandgap by modifying physical structures and chemical functionalities, using machine learning protocol, and calculating density functional theory (DFT) before preparing catalysts. This review will present the most recent contributions to modifying 2D materials to link the collective effort in developing photocatalysts for water oxidation. Furthermore, in the conclusion section, we will emphasize the ongoing work's perspective, challenges, and dimensions.

Keywords: Physical modification; Photocatalysis; Water splitting; Machine learning.
Received: 11 April 2022; Revised: 06 May 2022; Accepted: 17 July 2022.
Article type: Review article

1. Introduction

A continuous craziness for unconventional work by Andre Geim awarded him Ig Nobel prize on "Of Flying Frogs and Levitrons," for his 'silliest' experiment in 2000 but, 10 years later, in 2010 he was awarded Nobel prize for their ground-breaking discovery of graphene. Graphene is produced when the six-membered aromatic carbon rings are fused in a two-dimensional (2D) sheet to form an atom thin layer of 'zero-gap semiconductor material. The presence of excellent surface area (2630 m^2g^{-1}),[1] high Young's modulus (~1 TPa),[2] great optical transparency,[3] high room temperature carrier mobility (~10000 $cm^2V^{-1}s^{-1}$),[4] exceptional thermal conductivity (3000–5000 $Wm^{-1}K^{-1}$)[5] with a quantum hall effect[4] withdraw tremendous interests in many fields.[6-8] A craziness started a journey to make the thin carbon field, ultimately ending up in an emerging 2D material field in science. With such excellent features, material scientists started to extend and tune the properties further by exchanging some carbon atoms with electron-rich (N) or electron-deficient (B) atoms for generating graphitic carbon nitride (g-C_3N_4) or hexagonal boron nitride (*h*-BN) respectively. Inorganic chemists further accelerated this movement by preparing a series of 2D materials like transition metal or post-transitional metal-derived dichalcogenides (MoS_2, $MoSe_2$, WS_2, WSe_2), or black monoatomic phosphorus layer (phosphorene).[9,10] All these 2D layer materials are formed by strong intralayer covalent bonds and poor interlayer interactions like van der Waals interlayer or π-π staking. The advantage of the 2D photocatalyst is that a photocatalytic material can absorb the

[1] *Department of Chemistry, Malda College, Malda, West-Bengal - 732 101, India.*
[2] *Chemical and Biomolecular Engineering Department, University of Tennessee Knoxville, Tennessee 37996 USA.*
[3] *Functional Chromophores Group, International Center for Materials Nanoarchitectonics, National Institute for Materials Science, Tsukuba, Japan.*
[4] *Foundation of Physics Research Center (FoPRC), 87053 Celico, CS, Italy.*
[5] *International Institute of Invincible Rhythms, Churat Nala Road, Chakrail, Bhattakufer, Shimla 171006, Himachal Pradesh, India.*
**Email:* 2c.pathik@gmail.com (P. Sahoo)

maximum number of photons if it is spread as a thin layer in forming a 2D catalyst to carry out the reaction.

Despite the similarity in layered arrangement, their different atomic arrangements introduce unique chemical, catalytic, electronic, thermal, optical, and magnetic properties, offering a rich arsenal for a plethora of applications. Besides the chemical arrangement, lowering the size, typically below 20 nm introduces new properties like quantum confinement effects. When the particle size is further reduced and forms a new class of 0D materials, it behaves as a quantum dot with increased solubility and fluorescence properties and becomes accessible for doping different atoms. For further modification, researchers oxidize graphene by the hummers method and utilize the newly generated carboxylate functionalities to coordinate various reaction centers with further chemical modifications,[11] which could be implicated in multi-walled carbon nanotube as well.[12,13] This interest in 2D materials further spreads to the crystal engineering[14] society and the last decade witnessed the 2D metal-organic framework (2D MOF) and 2D covalent organic framework (2D COF).[15] For their intense knowledge of the structure designing principle for creating reaction centers, tuning bandgap, generating supramolecular voids, using light-harvesting groups, and post-synthetic modifications, a MOF can be converted into an excellent catalytic center or photocatalytic center.[16]

Inside a 2D lattice, a periodic movement of elastically arranged collective atoms or molecules has been named a phonon. It behaves like a quantized wave of sound. People working on condensed matter systems explore phonon systems in 2D materials to explain the thermal conductivity, electrical conductivity, neutron scattering-related effects, *etc*.[17] These phonons interact with the electron or light and came up with some unique features like tuning bandgap energy, conductivity, *etc*.[18]

For making a 2D material photocatalyst, the material should absorb the energy in the form of light and emits electron at a particular center by creating a positively charged hole under the local photoelectric effect. This electron travels through conducting the band and reaches the reaction centers for reducing a specific target. In the case of electronic devices, the electron is used to run a device. A serge for heterogeneous photocatalytic materials started with exploring varieties bottlenecked to the 2D physical shape and is now advancing the materials by further physical modifications and algorithmic predictions.

When a photon falls over a semiconductor, the electron from its valance band jumps over to the conduction band. The bandgap for the water oxidation catalyst lies between 2.0 - 3.0 eV (Fig. 1). A photocatalyst can be built with suitable catalytic reaction centers, an appropriate bandgap, and optimized semiconductor size with a modified 2D shape. Besides photons, thermal energy can also be harvested and used for driving nanobots. And in the future, one can employ it for water oxidation purposes.[19]

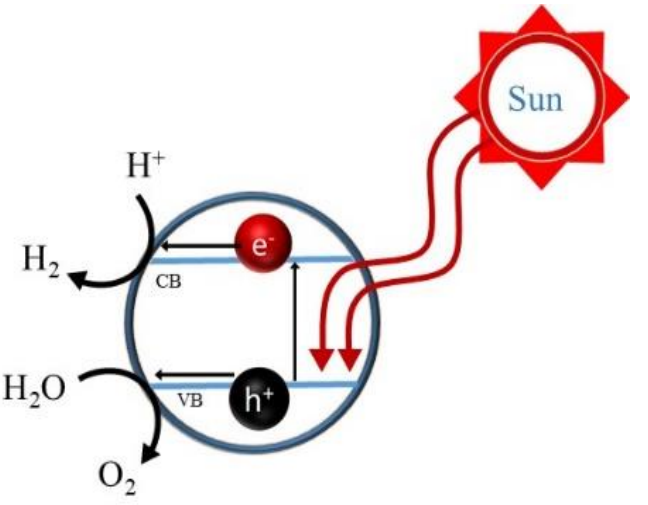

Fig. 1 A schematic presentation of the photocatalyst. When a photon falls over the valance band of the catalyst, the electron jumps to the conduction band, leaving a positive hole there. The positively charged valance band works as an anode, and water is oxidised to oxygen. At the conduction band, the proton accepts electrons and is reduced to hydrogen.

2. Physical modification in tuning chemical property

The last decade witnessed a strategic improvement in designing 2D materials. The linear photochemical response depends on the size of the optical band gap in determining the onset of optical excitation and the absolute energetic band edge positions in determining the reductive or oxidative property of the light-driven electrons and holes. Tunning such property can be possible by changing the material composition and particle size, modifying the surface chemistry, or exploiting electrostatic fields.[20] Some highly active catalysts are either confined in specific dimensions or designed differently to be available to reactant molecules to increase catalytic activity. Some physical parameters even can be changed to alter the catalytic property.

2.1 Floating sheet: Introducing advantages of homogeneous and heterogeneous catalysis

The floating strategies are developed to disperse the 2D heterogeneous catalyst materials homogeneously in a reaction medium. Because heterogeneous materials are insoluble in the solvent, it remains fixed for the duration of the reaction, and the reaction mixture must come into contact with it. However, the advantage is that heterogeneous catalysts are easily separable. On the contrary, homogeneous catalysts are reachable to every part of the reaction solution and simultaneously promote the entire solution to a product. At the same time, if the product is also soluble in the reaction solvent, it would not be easy to separate. To accumulate all the advantages described here and disadvantages to discard, we need to develop the floating catalyst, which can cover the reaction media volume but can be separated easily like heterogeneous catalysts (Fig. 2).

Urbonavicius *et al*. reported floating titanium dioxide

(TiO_2) as such photocatalyst for decomposition of methylene blue or inactivating Salmonella typhimurium.[21] They used nanocrystalline anatase TiO_2 to deposit on high-density Polystyrene by magnetron sputtering and the resultant 2D flake can float in the solution. In a separate study, Wang *et al*. loaded Polystyrene on the hollow glass microspheres surface by silane coupler, and then they precipitated amorphous TiO_2 through a hydrolysis reaction.[22] This hybrid system acts as a floating 2D catalyst and was used for degrading Rhodamine B and phenol under ultraviolet (UV) radiation or sunlight. These advantageous materials can also be used to generate hydrogen from water using solar energy. Lin *et al*. developed 2D amorphous nickel oxide (NiO) photocatalyst for H_2 evolution.[23] In addition to the advantages of the floating condition, the amorphous condition increases the surface area further. Such porous 2D floating catalytic systems are so advantageous that sacrificial agents might not always be needed. Liang *et al*. reported such floating 2D $MnIn_2Se_4$ nanosheets for water splitting purposes.[24]

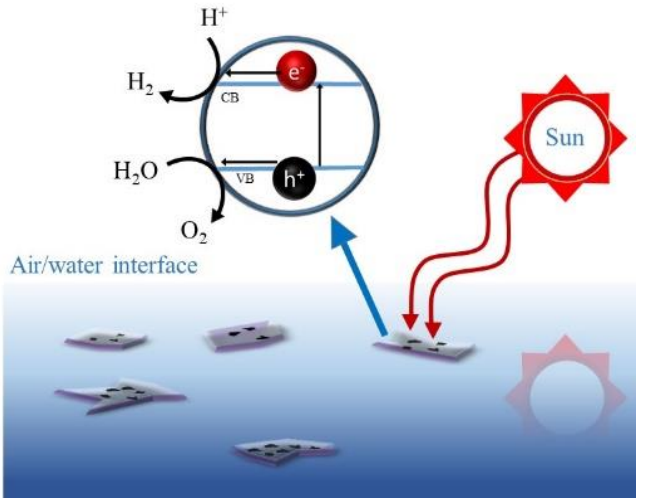

Fig. 2 A schematic presentation of floating catalyst in water. The porous or surface-modified 2D sheets can float all over in water. In the presence of sunlight, it can split water throughout the whole volume, similar to a homogeneous catalyst.

2.2 Coating a Homogeneous system over a heterogeneous surface

Heterogeneous catalysts can be homogeneously dispersed in the reaction medium by coating some soluble materials over the heterogeneous catalyst surface to make the reaction rate faster. Martínez-Prieto *et al*. ligated the platinum nanoparticle by long-chain N-heterocyclic carbine for carrying out the hydroboration reaction on phenylacetylene (Fig. 3).[25]

2.3. Confined catalyst under two-dimensional materials

Inorganic nanomaterials can be confined in low dimensional (0D-2D) materials to enhance the catalytic property further. This can be used both for electro and photocatalytic reaction purposes. The carrier confinement effect can be used to tune the bandgap and density of states while modifying the morphology of catalyst materials.[26] 2D catalyst materials can be confined basically by space-confined or surface-confined methods.[27] In the space confined method, the catalysts can be synthesized inside the 2D layers like layered double hydroxides (LDHs),[28-30] graphene, MXenes (2D material, derived from transition metal carbides, carbonitrides and nitrides), montmorillonite (MMT), and magadiite materials. Under suitable chemical conditions, the guest molecules form catalysts inside the 2D layers. In the case of surface-confined synthesis, the catalyst can be grown over the surface by using surface defects, functional groups, or surface atoms.

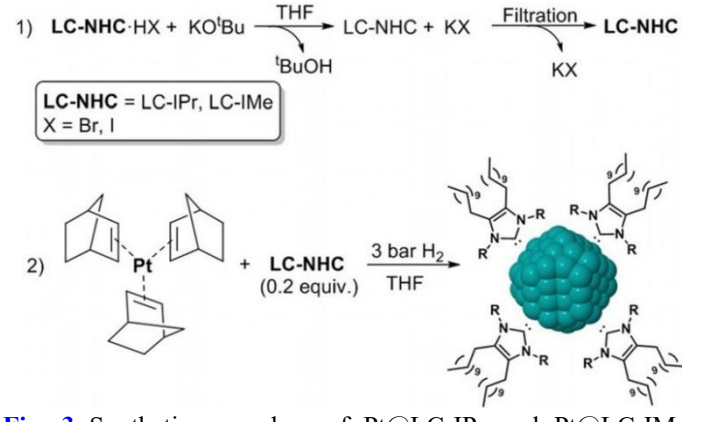

Fig. 3 Synthetic procedure of Pt@LC-IPr and Pt@LC-IMe. Reproduced with permission form [25], Copyright, 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The 2D special arrangement between the catalyst surface and 2D material creates a perfect microenvironment for confined catalysis experimentally and theoretically. Li *et al*., by using density functional theory (DFT) calculations, revealed that Pt (111) surface could be able to adsorb the atoms and molecules for the geometrical constraint and confinement field in the 2D space when the Pt (111) surface is confined in graphene.[31]

The confined catalysts can be used for various catalytic reactions. For example, growing defect-rich MoS_2 nanosheets inside graphene can be employed for removing smoke particles or other air-based toxic materials (Fig. 4).[32] The electron donor-acceptor inorganic/organic nanocomposites can be intercalated inside 2D layers for photocatalytic dye degradation.[33] They intercalated anions, copper phthalocyanine-3,4′,4′′,4′′′-tetrasulfonate and 3,4,9,10-perylene-tetra carboxylate co-intercalated inside the layered double hydroxides (LDHs) and used for dye degradation.

Spinel materials[13] are a class of inorganic oxide materials that can be exploited as suitable catalysts[11,12] and can be doped over oxidized graphene or carbon nanotube surfaces. When using graphene oxide, the spinel can be spatially confined inside the graphene layers. Yang *et al*. intercalated zinc ferrite ($ZnFe_2O_4$) inside graphene oxide flakes and exploited the material as a photocatalyst for methylene blue degradation under visible irradiation. Spinel-coated graphene has the potential for electrochemical or light-driven water splitting.[34]

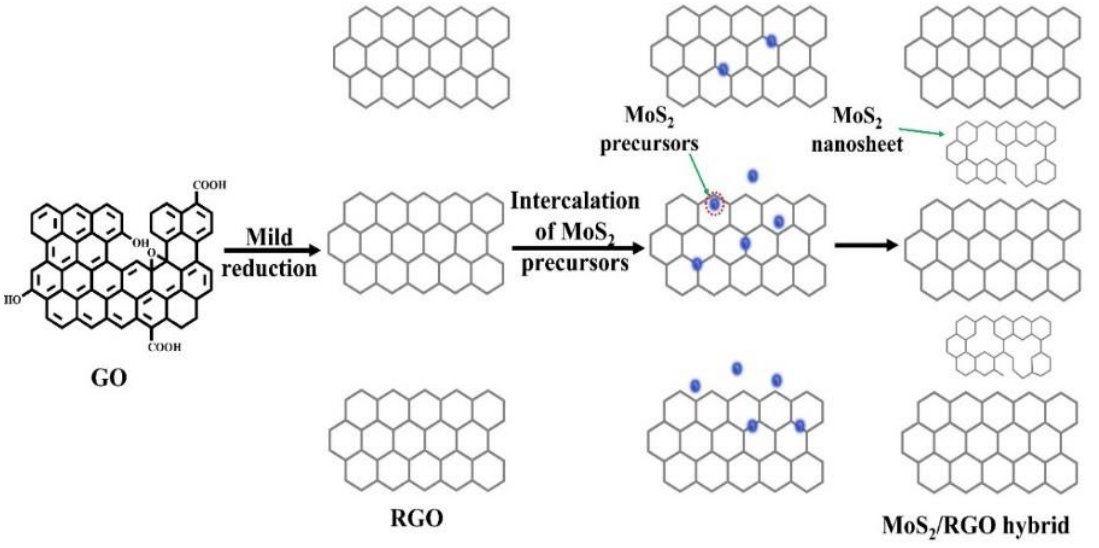

Fig. 4 Schematic presentation space-confined synthetic procedure of defect-rich MoS_2/RGO hybrid. Reproduced with permission from [32], Copyright 2016 American Chemical Society.

In their study, they used manganese ferrite. A cobalt ferrite-titanium dioxide composite ($CoFe_2O_4$–TiO_2) inside graphene oxide could also work as an efficient photocatalyst for overall water splitting purposes.[35]

Recently, single metal atoms are also used in confining them inside the 2D layers.[36] For example, Co atoms can be intercalated inside N-graphene and can be used as co-photocatalyst with CdS.[37] This Co intercalated N-graphene possesses an excellent ability for proton reduction and fast charge carrier separation, which resulted in an excellent amount of H_2 production of 1382 mmol/h.

However, graphitic carbon nitrides (g-C_3N_4) are widely used for single atom confined 2D catalyst preparation. These g-C_3N_4 are composed of synthetic polymeric layers[38] and packed by van der Waals bonding. This is an important class of semiconductor materials with the sp^2-π conjugated system[39] and can be employed as a photocatalyst,[40] electrocatalyst,[41] and organocatalyst.[42]

Li *et al*. showed confined Pt inside the g-C_3N_4 and exploited it for photocatalytic H_2 production.[43] This catalyst was synthesized in a liquid-phase reaction, using g-C_3N_4 and a Pt precursor, followed by annealing at 125 ºC for 1 h under an Ar atmosphere. Cao and co-workers prepared atomic Pd doped g-C_3N_4 catalyst for photocatalytic H_2 evolution.[44] This Pd/ g-C_3N_4 is quite stable enough for the strong synergic bonds between atomic Pd atoms and g-C_3N_4.

These kinds of confined catalysts also show the efficiency of hetero catalysts. Co(II) inserted Graphene Oxide shows efficiency as electrocatalysts at hydrogen evolution reaction (HER) reaction. In addition, hydrogen storing efficiency increases from 0.04wt% to 0.08wt% at 800 mmHg and 293K.[45]

2.4 Porous 2D materials

Porosity on 2D catalyst surface introduces high surface area, selective atomic deficiency, or interaction with reactant molecules driven photocatalytic and electrocatalytic properties. Porosity can be introduced by removing certain atoms from the lattice structure and can introduce N or P-type nature in developing semiconductors and enhance the catalytic property. Our recent study shows that oxygen atoms from ferrite lattice can be removed by sodium borohydride ($NaBH_4$) in ice-cold conditions to increase spinel's N-type character and catalytic activity.[12] In addition, the porous materials promote transporting electrons/holes by creating the local charged centres and also shorten the migration path distance of charge carriers between the charge producing centers and reaction centers in migration.[46] The longer charge carrier lifetime in the transient photoluminescence spectra confirms that porous 2D catalysts have higher charge carrier separation effectiveness.[47,48] Furthermore, the longer charge carrier lifetime is demonstrated by semicircular Nyquist curves with a smaller diameter in the electrochemical impedance spectra.[47,49] Hou *et al.* reported a highly porous system for photoelectrochemical water splitting (Fig. 5a)[50] Fang *et al.* also prepared the Ni-Co based porous nanosheet for efficient HER reaction. (Figs. 5b and 5c)[51]

2.4.1 Electronic Structure

The conduction band (CB) and valence band (VB) energy difference decides the required reaction energy for photocatalytic reactions. A more negative conduction band provides better reduction performance, while a higher positive value conduction band provides better oxidation performance. For instance, due to the hole's existence and quantum confinement effect, the conduction and the valance bands of single-layered porous g-C3N4 widened by 0.16 eV.[52] In mesoporous g-C_3N_4, the shifting of CB can promote a higher thermodynamic unfavorable reaction to favorable to exhibit photocatalytic hydrogen production. Liu *et al*. reported Co_3O_4 has 2 bandgap energies, which can be assigned as O^{2-}/Co^{2+} and O^{2-}/Co^{3+} charge transfer procedures, respectively.[53] The

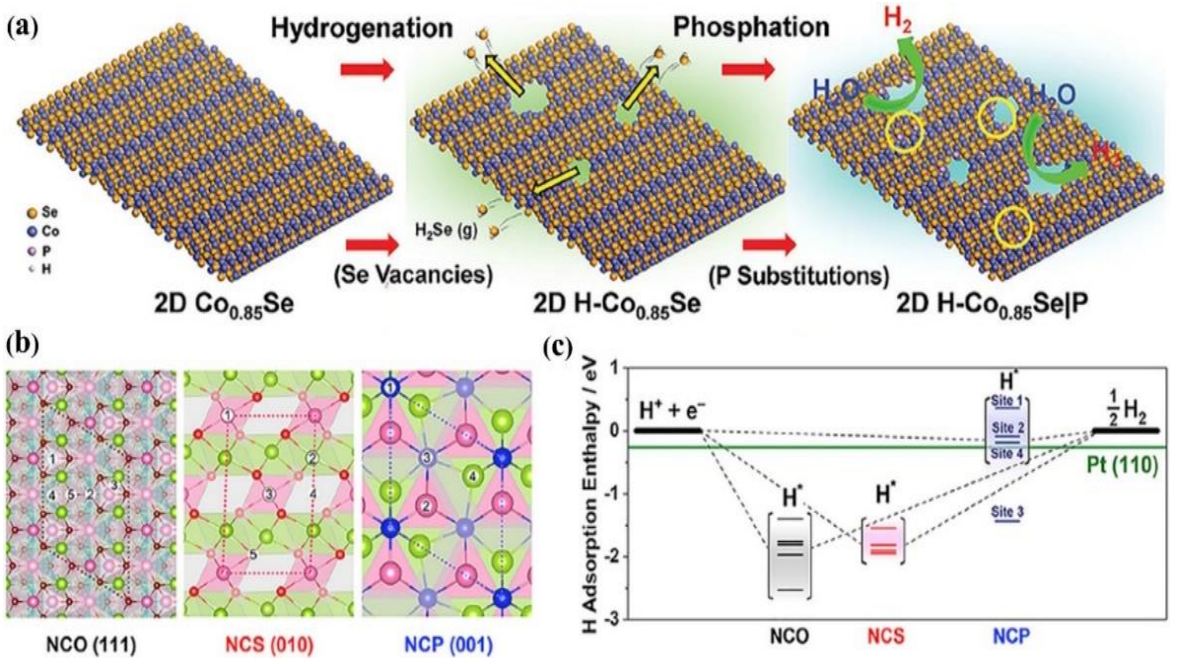

Fig. 5 (a) Synthetic procedure of porous 2D ultrathin H-$Co_{0.85}Se$|P. Reproduced with the permission from [50], 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (b) Distribution of atoms in crystal structure of NCO (111), NCS (010), and NCP (001). (c) DFT-calculated H_2 adsorption energy of NCO (111), NCS (010), and NCP (001). Reproduced with permission from [51] Copyright 2018 American Chemical Society.

porosity in Co_3O_4 increases the bandgap from 1.15 eV/2.14 eV to 1.49 eV/2.76 eV, with the shift of VB edge to the lower position, promoting the charge to a higher thermodynamic driving force in dye degradation. Furthermore, the pores promote the light scattering inside the hole and also enhance the light-harvesting through the elongated porous pathways.[54] The UV-Vis reflectance spectra from the porous $Zn_{0.5}Cd_{0.5}S$ shifted to a longer wavelength, depicting the enhanced light absorbance.[46] Liu and colleagues demonstrated that pores on WO_3 ultrathin nanosheets have greater light scattering and photon accumulation ability than nonporous nanosheets.[49]

2.4.2 Hydrogen Evolution Reaction (HER)

The HER is an uphill reaction where Gibbs free energy change is calculated as 237 kJ/mol or 1.23 eV.[55] When carbon deficient porous g-C_3N_4 was subjected to photocatalytic hydrogen production, it was seen that the porous counterpart was 20 times more efficient than the corresponding nonporous material.[47] In addition to the increased surface area, as shown earlier, the porosity absorbs light and improves photocatalytic efficiency. The photoluminescence emission and time-resolved photoluminescence spectra depict that the g-C_3N_4 had several emission centers. In addition, the quantum confinement effect in the nanosheets stabilizes the charge carriers. Most importantly, the 2D g-C_3N_4 exhibits a higher hydrogen production capability than the 3D porous g-C_3N_4. The protonated g-C_3N_4 nanosheets exhibit a higher quantum yield of 6.1% at 420 nm in comparison to bulk g-C_3N_4 and ultrasonically exfoliated g-C_3N_4.[56] Porous morphology in 2D nanosheet for $Zn_{0.5}Cd_{0.5}S$ enhances the H_2 evolution rate 2.5 times faster even after 15 hours compared to the nanorods morphology.[46]

2.5. Interfacial interaction

For the charge carrier of nanocomposites, interfacial interaction is crucial. The heterojunction between g-C_3N_4 and porous hexagonal boron nitride nanosheets can competently separate charge carriers and endorse electron transfer to the reaction centers.[57] In another study, 2D/2D heterojunctions between TiO_2 and g-C_3N_4 were created by three different methods (co-calcination of g-C_3N_4/TiO_2-cal; hydrothermally treated further to get O-g-C_3N_4/TiO_2, and by further acid, treatment to get H-g-C_3N_4/H-TiO_2) and exploited for H_2 evolution under visible light. The evolution rate was enhanced from 1.4- to 6.1-fold.[58] The heterojunction chemical bond Ti–O–N for g-C_3N_4/TiO_2-cal and O-g-C_3N_4/TiO_2 or the coulombic interaction in H-g-C_3N_4/H-TiO_2 quickens the electron transfer from the conduction band of g-C_3N_4 to the conduction band of TiO_2 and increase the efficient separation of e^-–h^+ pairs.

2.6 Bandgap tuning by solvent

Solvent plays a crucial in crystallization. The crystal structure can be altered by changing the solvents or the solvent ratio, which significantly impacts band energy.[59] The crystal structures of Cd-furan dicarboxylic acid-based MOFs can be modified by simply adjusting the solvent ratios in the solvothermal technique. Two MOF structures of $[Cd_3(FDC)_3(DMF)_4(H_2O)]$, and $[DMA]_2[Cd_3(FDC)_4]\cdot 2H_2O$ were prepared with a very small amount of water in DMF and

25% H_2O/DMF mixtures respectively. Both the structures have the trimer clusters as building units, but the 1st one is the furan dicarboxylate ligand to form a 2D structure, but for the 2nd one, clusters were linked linearly to form a 1D chain. The bandgap energy decreases from the first to the second structure. The lower band gap value of the second can be attributed to the infinite Cd-O-Cd arrangement, which splits the conduction band level to reduce the bandgap.

However, after forming the crystals or materials, besides electrons and holes, a solvent can still play a major role in tuning the bandgap. Water or other solvent molecules with arrangeable permanent dipoles can effectively screen electric fields by increasing the number of ions between the composite constituents. Voigt *et al*. demonstrated the solvent effect on their composite system (ZnS quantum dots and functionalized carbon nanotubes) in tunning the bandgap for the photochemical reaction.[18] These screening effects can be attributed to Debye-Hückel–approach.

2.7. Thickness of 2D materials

When 2D materials are formed by staking several layers by in-plane covalent or coordination bond and inter-planner van-der Walls' interaction and individual layers can be exfoliated by several techniques.[60,61] Both theoretically and experimentally, it can be shown that the band structure of these 2D materials clearly depends on the thickness (or the number of monolayers). With decreasing number of monolayers, the valence maximum point gets shifted in the Brillouin zone and the bandgap increases.[62-65] Fig. 6a shows that the transition of a bulk molybdenum sulfide (MoS_2) with an indirect bandgap of 1.20 eV to the direct bandgap of 1.90 eV appears when the thickness of MoS_2 reduces to a monolayer as verified by theoretical calculations and experimental optical absorption spectra. At the Brillouin zone, the valence band maximum at the Γ point moves to the K point (Fig. 6b). This phenomenon of bandgap crossover is a well-studied,[55,62-65] and photoluminescence (PL) quantum yield got 10^4 -fold enhancement in the case of monolayer MoS_2 (Fig. 6c).[62] Such bandgap crossovers were also reported in $MoSe_2$, $MoTe_2$ (molybdenum ditelluride), and WS_2 (Tungsten disulphide).[60] Basically, the semiconducting compounds of MoX_2 and WX_2 classes are expected to show a similar transformation of indirect to direct-bandgap, within range of 1.1-1.9 eV bandgap energy with decreasing layer number.[60] Studies showed that bottom-up synthesis is a better way of controlling the number of layers than exfoliation from parent bulk material. Chemical vapor deposition (CVD) is a very efficient technique in growing large monolayers of MoS_2, WS_2, $MoSe_2$, and WSe_2.[66-73] However, the molecular-beam epitaxy (MBE) method is the most sophisticated way of controlling the layer number of $MoSe_2$, where a single film can be grown layer-by-layer for 8 times.[74] The bandgaps and their light absorption properties as consequent can be tuned by adjusting the thickness of the 2D sheets.[75,76] The ultrathin nature of sheets reduces the recombination probability between electrons and holes.[77,78] By reducing thickness, the formation of ultrathin sheets increases the surface area and exposes the active sites to promote photocatalytic reactions.[79]

2.8. Defects Engineering

Constructing surface defects over the 2D photocatalyst by doping heteroatoms, creating hole by removing atoms or introducing functional groups can be an efficient strategy for improving photocatalytic activities.[80-88] The defects at the surface make the 2D sheets more conducive to the use of holes and photoelectrons in reducing and oxidizing the elements.[82] The electronic effects in defects reduce the HER and OER overpotentials[89] by improving the number and conductivity of photogenerated carriers. Defects create more catalytic centers or active sites to accelerate the reaction rates.[80] Defects also help absorb photons to promote the reactions.

Zheng *et al.* generated the point defects by developing selenium vacancy, diselenium vacancy, platinum vacancy, and diplatinum vacancy, which enhance the photocatalytic water-splitting efficacy of $PtSe_2$ monolayers.[90] On the other hand, by introducing hetero atom-like Pd into $PtSe_2$ layers, Ma *et al.*[91] enhance the HER efficiencies.

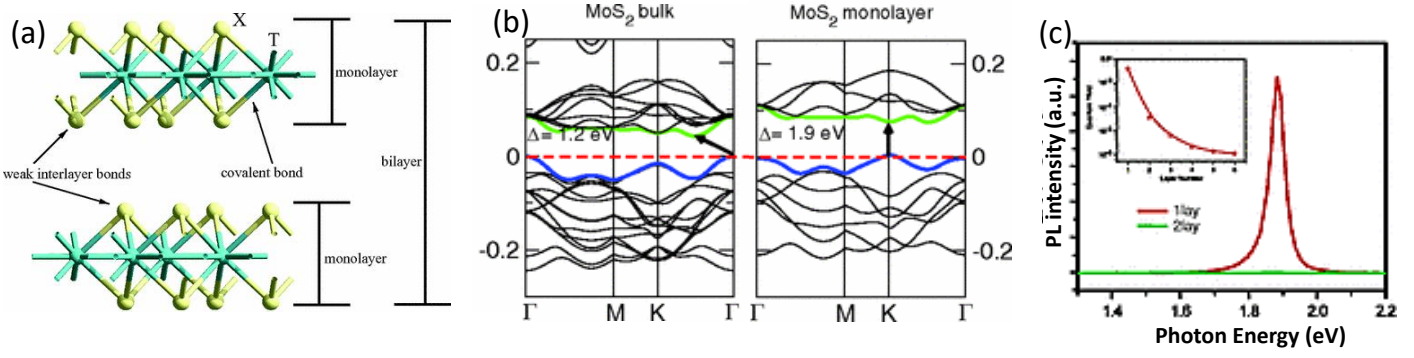

Fig. 6 (a) The atomic structure of layered TMDs of TX2 type (where T is transition metal and X is chalcogenide). (b) Band structures of MoS_2 in bulk (left) and monolayer (right) were calculated by the DFT method. Reproduced with permission from [64], Copyright 2011 American Physical Society (c) Photoluminescence spectra of MoS_2 (mono and bilayer). (Inset: With an increasing number of layers of MoS_2 quantum yield decreases. Reproduced with permission from [62], Copyright 2010 The American Physical Society.

2.9. Strain Engineering

The tensile or compressive strain can fine-tune the electronic structure of the surfaces by changing the interatomic distances at the 2D surface.[92-93] The strain effect can not be formulated by any equation as it varies with the local symmetry and the specific bonding of certain ions. Simultaneously it affects the electronic structure of the materials' surface. Single-layer sheets give better flexibility and can withstand a higher mechanical strain.[94,95] This surface strain tuning approach is another useful way to control the catalytic activities by varying the orbital overlap in catalysts.[96] In addition, the surface strain does not alter the catalyst composition,[97] which benefits in calculating and forecasting the influence of lattice strain for photocatalytic water splitting[98] through DFT calculation. Lattice strain, for example, in 2D transition-metal complexes, noble metals, perovskite oxides, and heterostructure, can influence a lot of potentials that change photocatalytic efficiency for water splitting[99-107]

3. Machine Learning

Besides experimental trials and errors, computational modeling like molecular dynamics (MD) or density functional theory (DFT),[108] machine learning protocol comes to predict material properties inexpensively through employing algorithms. This model predicts electronic properties, bandgap in developing heterojunction optical devices, solar cells, or photocatalysts. We can apply machine learning to create photocatalyst with specific precession since the bandgap in such materials plays a significant role in predicting the field of usage[109]. Thus, the time behind developing a brand-new useful catalyst can be minimized. Nowadays, various research groups are using machine learning algorithms for different areas of materials science. A self-adaptive differential evolution algorithm is used by Wang *et al*. in optimizing a reduced mechanism of 2-Butanone.[110] Zhang *et al*. came up with an overview of machine learning methods for predicting the thermal conductivity of different alloys, compounds, composites, and alloys.[111] Pilania *et al.* combined linear least square regression with kernel ridge regression in the bandgap prediction of double perovskites.[112] Ward *et al.* created a random forest technique for partitioning data into different groups to improve predictive accuracy to develop machine-learning-based models faster for applications.[113] Their method is useful in predicting diversified properties like glass-forming ability or bandgap energy for different crystalline or amorphous materials. A few ongoing methods employed in this study are random forest, linear Lasso (Least Absolute Shrinkage and Selection Operator) and Ridge regression, Gaussian process regression (GPR), support vector regression (SVR), and artificial neural network (ANN).[114] Recently, Palkovits have been used as an artificial neural network, reinforcing the vector regression and *k*-nearest neighbour regression in developing the water oxidation catalysts.[115] They showed by calculating metrics that support vector regression is the best-performing algorithm. However, the choice of algorithm is ruled only by the data. Jiang *et al.* developed a new machine learning (ML) model to determine the activities of different metal oxide-based photocatalysts on a series of contaminants.

The encoded metal oxide structure through a crystal graph convolution neural network (CGCNN).[116] The organic molecular structure is encoded through digital molecular fingerprints (MF). Finally, the CGCNN, MF, and the light are used as input at an artificial neural network (ANN) to build the Convolutional Neural Network - Molecular Fingerprints-Artificial Neural Network (CGCNN-MF-ANN) model (Fig.7).

Here the photocatalyst crystals are encoded through Crystal Graphic Convolutional Neural Network (CGCNN). Contaminants are represented through Molecular Fingerprint (MF), where ANN stands for artificial neural network.

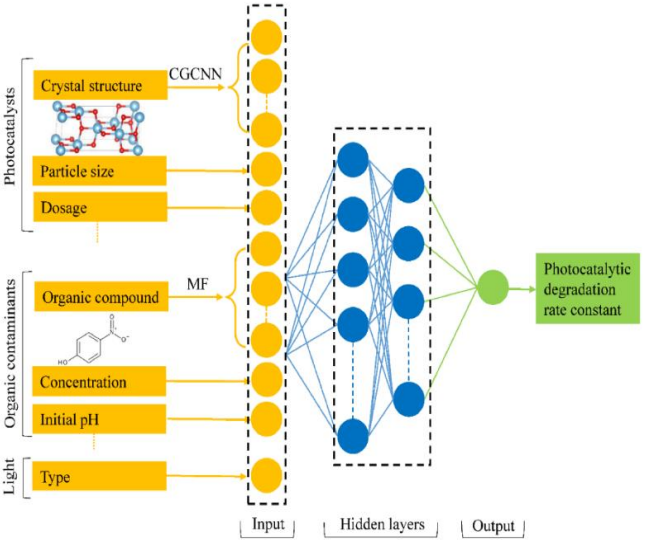

Fig. 7 Schematic presentation of CGCNN-MF-ANN model. Here the photocatalyst crystals are encoded through Crystal Graphic Convolutional Neural Network (CGCNN). Contaminants are represented through Molecular Fingerprint (MF), where ANN stands for artificial neural network. Reproduced with the permission from [116]. Copyright 2021 @MDPI.

4. Conclusions, Perspectives and Challenges

This review offers a brief synopsis of the physical functionalization and algorithmic prediction of different types of 2D materials for photocatalytic water oxidation. A wide range of materials like TMDs, MXenes, graphene, carbon nitride, boron nitride, MOFs, COFs, perovskite nanosheets, nanoheterostructure composites, *etc*. are discussed here with their further physical modification on their 2D shape. However dense surface defects are hard to avoid. Recently, people are further modifying the 2D photocatalysts to increase the photocatalytic efficiencies. Several protocols are used to ensure the availability of the 2D heterogeneous catalysts in all parts of the reaction solution. By coating the 2D materials on floating materials or by introducing a long chain over the 2D surface, a catalyst can float in the solution to enhance the reaction rate. Recently, templates have been used to confine the catalysts in 2D shape to improve the photocatalytic

property. Sometimes, for enhancing the surface area, making 2D materials amorphous is very crucial and for such purpose, by etching the surface, some atoms from the 2D lattice can be removed to introduce the porosity. The photocatalytic property can be adjusted by adding physical interfacial interactions in altering the physical property. The heterojunction between two materials in a 2D composite catalyst can separate the charge carriers competently and endorse the transfer of an electron to the reaction centers. The thickness of 2D materials also plays a central role in accelerating the photocatalytic reaction rate. Besides the physical modification over the 2D catalysts, by selecting the appropriate solvent molecules, the bandgap of the catalysts can be further tuned to enhance the catalytic property. We also emphasize the crystal engineering approach in designing the MOF-based photocatalysts, which could be very useful for crystal engineers looking to employ their systems in water oxidation. A variety of different 2D materials, material-wise preparative protocols, reaction mechanisms are also discussed briefly for the betterment of understanding the complete process to the readers. A journey from finding the chemical property in materials started generating the proper shape and dimension in it and further presently modifying the materials physically for employing them in heterogeneous water oxidation. However, crystal engineering and machine learning protocols are newly adapted to make the process error-free in designing catalysts.

Designing multipurpose photocatalysts for synthesizing different products from a certain chemical solution will be expected for designing smart industrial or household devices. By exploring crystal engineering and time crystal engineering,[117] a time-space arrangement in reaction–catalysis can introduce fractal event organizing nested time crystal branch in picking out a desired product from the competitive synthesis mode according to our requirements.[118]

Thus, this research is reached at such a level that developing a catalyst by a single person becomes impossible. A good team effort involving various experts such as catalysts, crystal engineers, machine learning, and material science will reduce the effort required to develop more efficient water oxidation catalysts for the benefit of civilization.

Acknowledgement
PS acknowledge NIMS, Japan.

Conflict of Interest
The authors declare no conflict of interest.

Supporting information
Not applicable.

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Author information

Indrajit Chakraborty *received his PhD in Organic Photochemistry from the Indian Association for the Cultivation of Science, India in 2009. He then became an Assistant Professor at Surendra Institute of Engineering and Management in Siliguri, India. One year later, he became an assistant professor at Kalinga Institute of Technology in India (2010 to 2015). He is currently employed as an Assistant Professor at Malda College in West Bengal, India. His main areas of interest in research are organic synthesis, material science, and photochemistry.*

Zhanhu Guo *an Associate Professor in the Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, USA. He obtained a Ph.D. degree in Chemical Engineering from Louisiana State University (2005), and then received three-year (2005–2008) postdoctoral training from the Mechanical and Aerospace Engineering Department at the University of California Los Angeles. Dr Guo chaired the Composite Division of the American Institute of Chemical Engineers (AIChE, 2010–2011). Dr. Guo is the Lifetime Fellow of Indian Chemical Society (ICS, 2020) and Fellow of the Institute of Materials, Minerals and Mining (FIMMM, 2021). Dr. Guo is the director of the Integrated Composites Laboratory. His current research focuses on multifunctional nanocomposites for energy, electronic and environmental applications.*

Anirban Bandyopadhyay *is a Principal Research Scientist at the National Institute for Materials Science (NIMS), Tsukuba, Japan. Ph.D. in IACS, Kolkata, 2005. 2005-2008 ICYS research fellow at ICYS, NIMS, Japan. In 2008, joined as a scientist at NIMS, working on design-synthesis of brain-like organic jelly, written a book "Nanobrain: The making of an artificial brain from a time crystal", 2020. 2013-2014 visiting scientist at the Massachusetts Institute of Technology (MIT), USA. Hitachi Science and Technology award 2010, Inamori Foundation award 2011–2012, Kurata Foundation Award, and Sewa Society international member, Japan.*

Pathik Sahoo *did his PhD from the Indian Association for the Cultivation of Science, India on 'Designing Low Molecular Weight Gelator: A crystal Engineering Approach' in 2012. He works at NIMS, Japan on Gel Computation, 3D holographic lens, developing supramolecular gel-based artificial brain, and time-crystal engineering in chemical reactions, etc. He is the visiting Professor at the Foundation of Physics Research Center (FoPRC), Italy. Besides pursuing research, he also plays roles as editor, and guest editor in some journals and delivers invited talks at several renowned research Institutes on the supramolecular artificial brain and supramolecular gel-based invariant computation, etc.*

