First-principles simulations on 2D materials toward energy applications

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1. Background and Research Purpose:

Developing clean and sustainable energy sources is one of the particular challenges to overcoming the energy crisis and the harmful environmental impacts of fossil fuels. Photocatalysis and electrocatalysis have emerged as promising technologies to produce the cleanest hydrogen fuel,[1-3] which is critical for decarbonization and net-zero world targets (Figure 1).

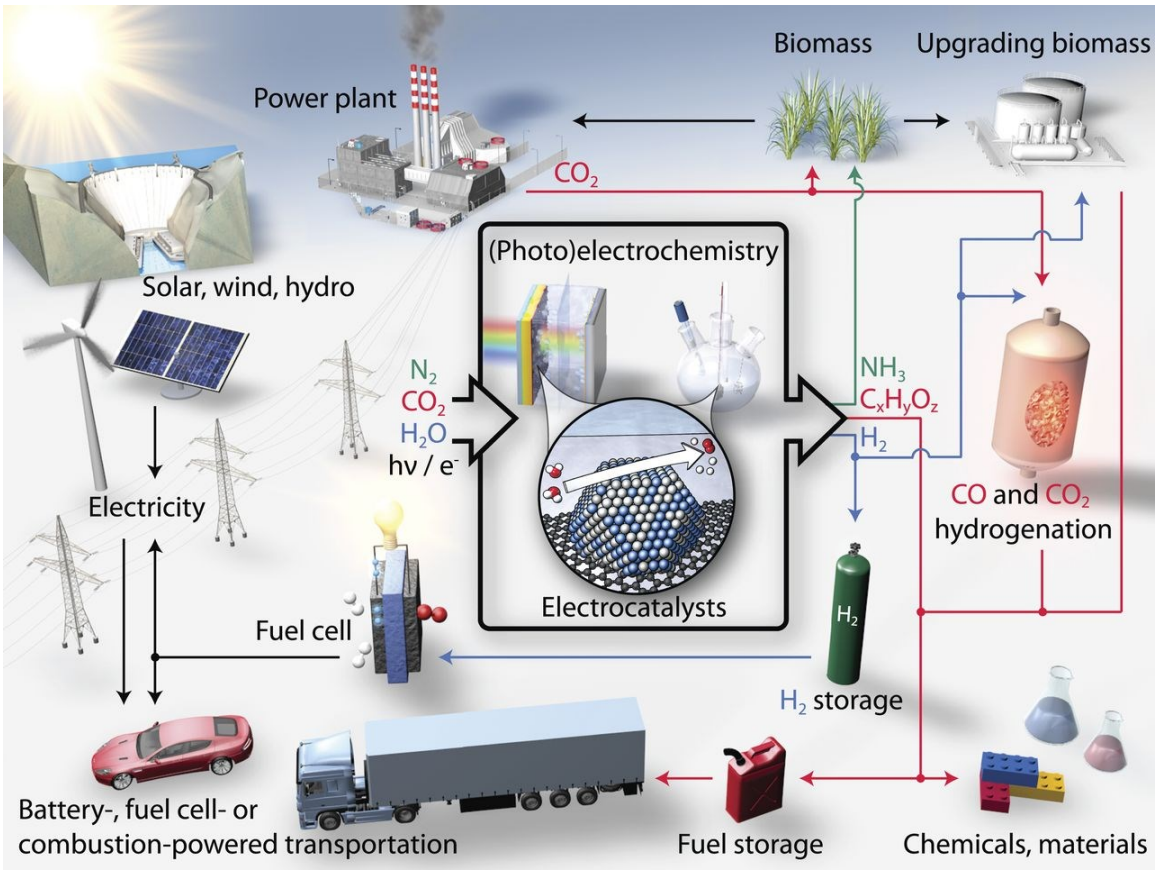

Fig. 1 Schematic illustration of sustainable clean energy future based on catalysis.[2]

Two-dimensional (2D) materials are a revolutionary class of materials with unique properties that are distinct from their bulk counterparts (Figure 2).[4-6] Compared to conventional bulk materials, 2D materials possess a high specific surface area, a high surface-to-volume atomic ratio, and tunable properties. Hence, 2D materials with remarkable physicochemical and catalytic properties have recently garnered much attention in energy-related fields.[7-10]

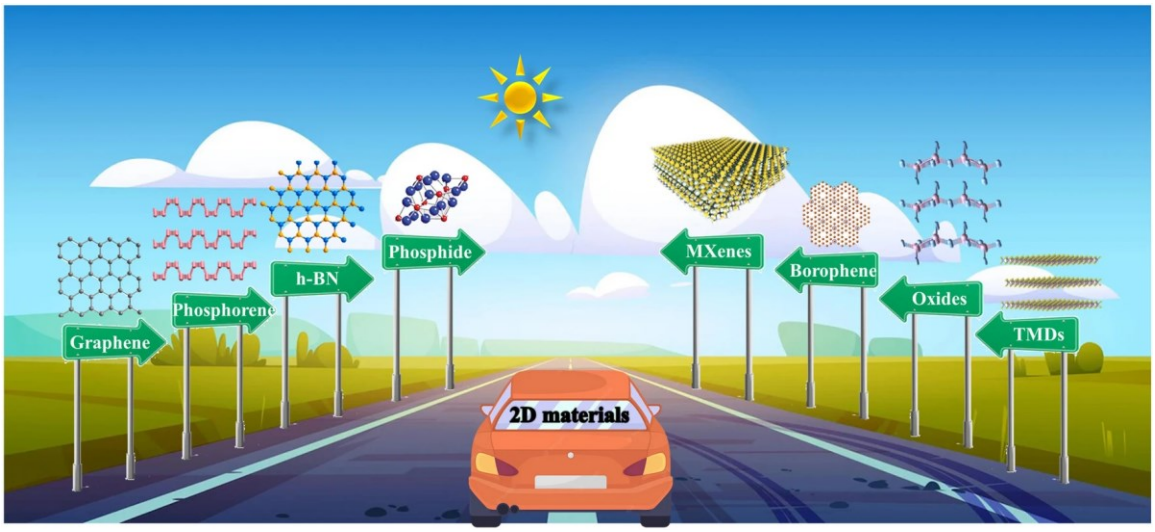

Fig. 2 Schematic illustration of the development of 2D materials.[5]

However, the intrinsic physicochemical properties of pure 2D materials greatly limit their wide range of energy-related potential applications. The key challenge in this field is developing highly efficient 2D catalysts. In particular, one of the main scientific issues is that the basal plane of most 2D materials in their pristine form is chemically inert, thus being inefficient catalysts. Fortunately, surface modification strategies such as doping, vacancies, and their combinations of defects can tailor the intrinsic properties of 2D catalysts, opening new pathways in energy-related fields.[7-11] These strategies can be optimized by fine-tuning the concentration and arrangement of defects, which is challenging in the experiment but enabled by theoretical methods.[7,11] Quantum-mechanical first-principles calculations, based on periodic density functional theory (DFT) and perturbation theory (DFPT), are effective computational methods for investigating the fundamental features of 2D materials, providing atomic-scale insights into their physical and chemical properties.[7-12] It is still necessary for comprehensive first-principles simulation studies on 2D materials via surface modifications toward specific energy applications.

My research goal is to develop highly efficient 2D catalysts using first-principles simulations. To achieve this goal, I first intend to consider potential modifications to 2D materials:

a) **Vacancies:** vacancies are the most commonly observed defect in 2D materials during the fabrication and processing stages. As demonstrated in our previous studies, creating vacancies within the 2D material can tailor its physical and chemical properties, acting as active sites for reactions and possibly enhancing the overall catalytic performance.[6,7]

b) **Doping:** our previous studies have shown that introducing dopant atoms to the surface of pure 2D materials is an effective strategy for the modification of electronic properties, further affecting catalytic properties for both photocatalysis and electrocatalysis. Choosing the proper dopants and concentration has greatly altered the electronic structure and generated active sites for a specific reaction, suggesting better performance in energy applications.[7-11]

c) **Dual defect:** our previous work on photocatalytic water splitting introduced a new strategy called a dual defect in which doping and vacancies are applied simultaneously as synergetic defects (Figure 3).[7] In particular, this potential strategy greatly improved optical and electronic properties as well as enriched active sites on the basal plane of 2D material, resulting in enhanced light harvesting and electron-hole separation, which are the key factors in solar-to-hydrogen efficiency. We believe that the dual defect strategy can be potentially applicable for developing the catalytic characteristics of 2D materials for energy applications.

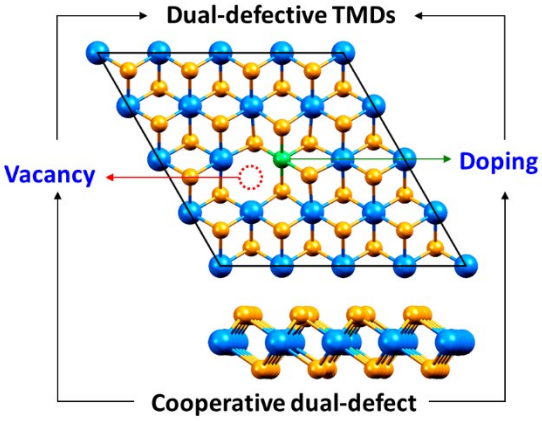

Fig. 3 Dual Defect Strategy. This method integrates doping and vacancies as a cooperative dual defect to enhance the catalytic properties of 2D materials for energy applications.

Then, I aim to apply these surface modifications to three prominent classes of 2D materials (Figure 4) including transition metal dichalcogenides (TMDs), transition metal carbides/nitrides (MXenes), and metal-organic frameworks (MOFs) because of their relatively low cost, abundance, and nontoxicity. These low-dimensional materials exhibit remarkable electronic, optical, and catalytic characteristics,[7-16] making them attractive for efficient energy conversion processes. It is worth noting that 2D semiconductors with a suitable bandgap are essential in photocatalysis, while 2D metals with high conductivity are crucial in electrocatalysis.

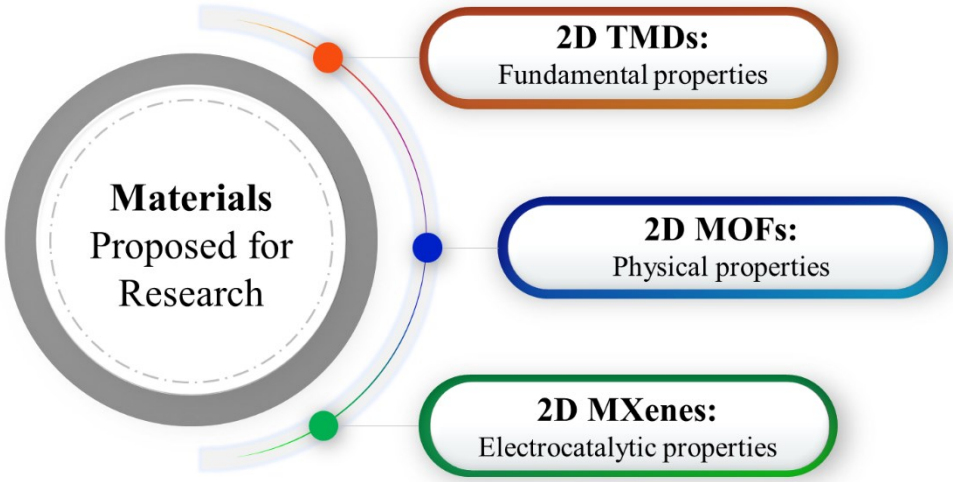

Fig. 4 The proposed 2D materials for future research.

Subsequently, I aim to investigate and uncover promising 2D catalysts that will be enabled to develop via defect engineering to solve key issues in the catalytic properties of 2D materials. For this purpose, I focus on the energy conversions that are active areas of my research interest:

a) Water splitting: Solar-light-driven photocatalytic water splitting based on a semiconducting photocatalyst has emerged as a promising technology to produce both oxygen and hydrogen fuel (Figure 5). Photocatalytic water splitting covers complex interplays between photophysical and chemical processes, as follow: First, the semiconducting photocatalyst absorbs a photon from sunlight with energy equivalent to its band gap. Second, an electron is excited from the valence band to the conduction band, generating electron-hole pairs in the photocatalysts. Third, the electron-hole pairs transfer to the surface of photocatalysts. Finally, the redox reaction occurs on the surface, generating hydrogen and oxygen.

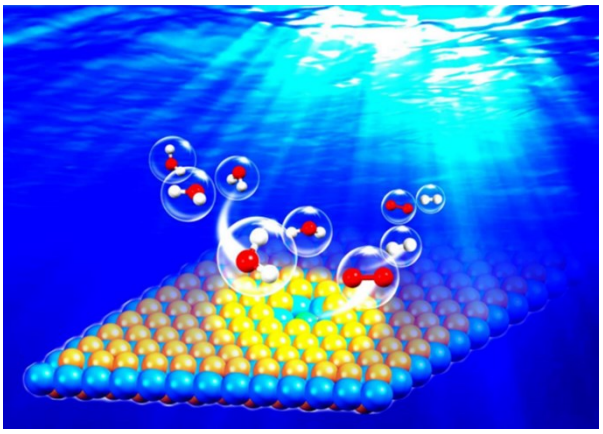

Fig. 5 Schematic illustration of water splitting on the defective 2D material.

In principle, an efficient photocatalyst for overall water splitting is required to meet three major criteria: (i) the photocatalyst should be a semiconducting material with a moderate bandgap in the range of 1.2–3.0 eV to harvest a significant portion of solar energy; (ii) sunlight-driven photogenerated carriers—electrons and holes—in a semiconducting catalyst are necessary to promptly transfer and efficiently separate to prevent both bulk and surface charge recombination; and (iii) more importantly, the photocatalyst must exhibit an appropriate band alignment. The valence band maximum (VBM) must be lower than the oxidation potential of O_2/H_2O (5.67 eV) to first split water, and the conduction band minimum (CBM) should be higher than the reduction potential of H^+/H_2 (4.44 eV) to further produce hydrogen, respectively, as illustrated in Figure 6. Using surface modification, our study focuses on developing an efficient 2D photocatalyst that can overcome all major criteria for overall water splitting.

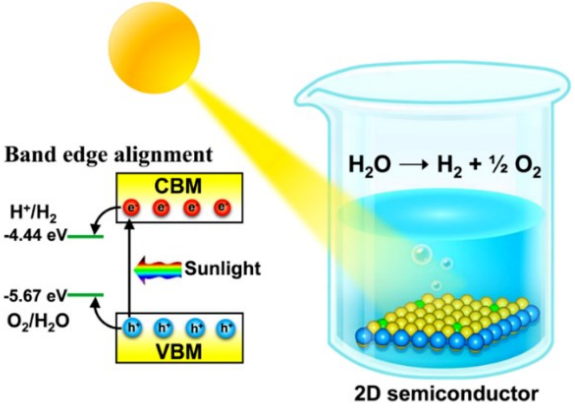

Fig. 6 Schematic illustration of photocatalytic mechanism on 2D materials.

b) **Hydrogen Evolution Reaction (HER)**: The hydrogen evolution reaction through electrocatalysis is an economically and environmentally optimal way to produce hydrogen, the cleanest fuel with high energy density, recyclability, no pollution, and no greenhouse gas emissions. In general, the HER is determined by a three-state profile: (i) initial state $H^+ + e^-$; (ii) an intermediate adsorbed H*; and (iii) a final product $\frac{1}{2}H_2$. The Gibbs free energy (ΔG_{H^*}) of the intermediate state is typically considered a core indicator to define decent catalysts. A highly efficient catalyst for HER should have a near-zero value of ΔG_{H^*}. The main challenge is to develop an efficient 2D electrocatalyst to meet this criterion for HER. Using the dual defect strategy, our first-principles study has developed an efficient 2D electrocatalyst with a near-zero ΔG_{H^*} for HER (Figure 7).[8,9] This strategy offers a new perspective on improving the catalytic properties of other 2D materials.

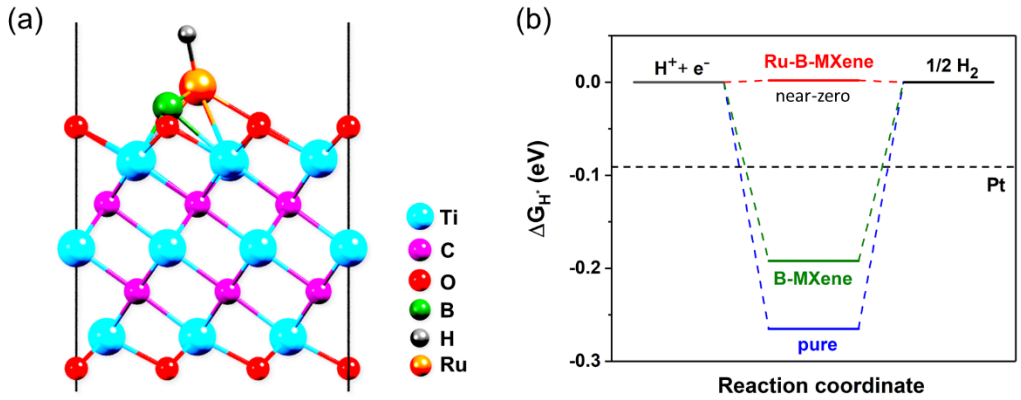

Fig. 7 Dual-defected MXene exhibits a near-zero value of Gibbs free energy, indicating an efficient 2D electrocatalyst for the HER.

c) **Oxygen evolution reaction (OER)**: OER is crucial for developing sustainable energy conversions. However, OER faces the challenge that oxygen molecules transfer via the intermediate species of OH, O, OOH, and O_2, slowing down the reaction mechanism. It implies that the oxygen reaction can proceed more efficiently in the presence of appropriate catalysts only. Notably, O_2 has two unpaired electrons and is in a triplet state as paramagnetic at the ground state. However, the catalytic role of spin, a fundamental quantum characteristic of electrons, remains greatly elusive. It calls for comprehensible research of spin-induced oxygen electrocatalysis. Our study investigates how the spin enhances the OER performance of 2D materials using spin-polarized first-principles calculations.

2. Objectives

The ultimate aim is to resolve the key issues to be faced in the field of 2D materials for energy applications. To achieve the objectives, I will conduct the research in the following sequences.

a) To explore the structural properties of proper 2D materials via defect engineering:

- Search for proper 2D materials for a purpose.
- Modify the selected 2D material via defect engineering for a purpose.
- Investigate the structural properties of defect-modified 2D materials.
- Predict the stability (energetical and dynamical stabilities) of defect-modified 2D materials.

b) To investigate the electronic properties of defect-modified 2D materials:

- Calculate the band structure, DOS, and charge transfer of the selected 2D materials.
- Determine the presence of bandgaps and examine their direct or indirect nature.
- Define the expected catalytic properties, based on the electronic structure of modified 2D materials.

c) To study the catalytic properties of defect-modified 2D materials:

- Estimate the adsorption energy of relevant absorbents on the surfaces of 2D materials.
- Evaluate the Gibbs free energy to elucidate the reaction mechanisms of a specific catalytic process.

d) To establish the structure-property relationship of defect-modified 2D materials:

- Establish a relationship between geometrical and electronic properties.
- Clarify the relationship between structural, electronic, and catalytic properties.
- Determine the critical parameters regulating efficient catalytic characteristics.

- Propose a guiding principle of defect-assisted surface modification that enhances the catalytic properties.
- Apply this principle to other 2D materials (or beyond) for energy applications.

Furthermore, I intend to provide the experimental groups with computational supports (geometrical structure, electronic structure, determination of catalytic active sites, interpretation of reaction mechanisms, first-principle simulation of spectroscopy, first-principle simulation of physical properties, and so forth).

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