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MXene-Based Plasmonic Heterostructures for Photocatalytic Water Splitting: A Mini Review

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Abstract: ***Photocatalytic water splitting is a promising approach for sustainable hydrogen production using solar energy; however, this process is limited due to rapid charge recombination and sluggish oxygen evolution reaction (OER) kinetics. Conventional catalysts such as IrO_2 and RuO_2 show excellent activity but are expensive and scarce. In this review article, the focus is mainly on $Ti_3C_2T_x$ MXene-based plasmonic heterostructures integrated with carbon–nitrogen semiconductors (e.g., g-C_3N_4 and C_2N) to enhance photocatalytic performance. The localized surface plasmon resonance (LSPR) of MXenesimprove light absorption according to previous studies, promote hot carrier generation, and facilitate charge separation. Every material is made up of the special periodic arrangement of atoms in definite directions or paths. Therefore, stabilities and inherent properties of materials depend on the atomic arrangements. Hence, we have briefly discussed the computational techniques can be used for such study. This study aims to investigate electronic structure, optical properties, and catalytic activity. The work will identify key descriptors such as adsorption free energies, band alignment, and plasmonic response, ultimately providing design guidelines for efficient, low-cost photocatalysts.***

Keywords: MXene, $Ti_3C_2T_x$, Plasmonics, LSPR, Photocatalysis, Water Splitting, DFT, TDDFT, g-C_3N_4, Heterostructures

I. INTRODUCTION

The global transition toward clean and sustainable energy systems has spurred research into solar energy conversion technologies. Among these, photocatalytic water splitting offers a direct and environmentally friendly pathway for hydrogen production. Despite decades of research, practical execution remains challenging due to inefficient light utilization, rapid recombination of photogenerated charge carriers, and slow surface reaction kineticsparticularly for oxygen evolution reaction (OER).[1-3]Benchmark catalysts such as IrO_2 and RuO_2 exhibit excellent OER activity but suffer from high cost and limited availability, restricting their large-scale application.[4]Consequently, there is a pressing need to develop alternative materials that are both efficient and economically viable.Plasmonic nanostructures have emerged as a promising solution due to their ability to enhance photocatalysis through localized surface plasmon resonance (LSPR)[5] LSPR leads to strong light absorption, generation of energetic (hot) carriers, and local electromagnetic field enhancement. Simultaneously, MXenes, a class of two-dimensional transition metal carbides/nitrides, have attracted attention due to their metallic conductivity, tunable surface terminations, and strong light-matter interaction. In particular, $Ti_3C_2T_x$ MXene[6]exhibits broadband absorption in the visible-near-infrared region and supports plasmonic excitations with relatively long carrier lifetimes.This review suggest other researcher if we combine MXenes with carbon-nitrogenbased semiconductors to form heterostructures that synergistically improve photocatalytic efficiency.

II. FUNDAMENTALS OF PHOTOCATALYTIC WATER SPLITTING

Photocatalytic water splitting proceeds through three fundamental steps:

Solar-light-driven water splitting using particulate photocatalysts is very promising method to convert solar energy into chemical energy. It is an artificial photosynthesis process which is similar to photosynthesis in plants[7-8]. A general photocatalysis process involves some basic key steps as shown in figure 1.2.

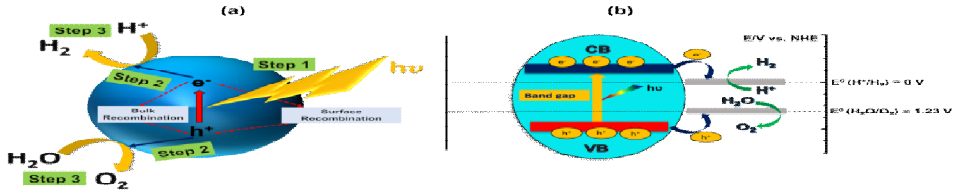

Figure 1: (a) Schematic representation of basic photocatalytic water splitting process and (b) semiconductor-based water splitting method.

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The photocatalysis process initiates by light irradiation followed by production of photoexcited charge carriers [electron (e^-) and hole (h^+)]; (ii) second step is the separation of these charge carriers which further migrate on to the surface, simultaneously one competitive action also happens which is bulk and surface recombination (photogenerated charge carriers recombines within a few nanoseconds and dissipates energy in the form of heat); (iii) in the last step, these photogenerated e^- (h^+) can further reduce (oxidize) water to produce hydrogen and oxygen, respectively [8-9]. In terms of thermodynamics, overall water splitting is endergonic reaction with standard Gibbs free energy change (ΔG^0) +237 kJ/mol as represented in equation (1):[10-11]

$$H_2O \rightarrow 1/2O_2 + H_2; \Delta G^0 = 237\ kJ/mol;\ \Delta E^0 = 1.23\ V \quad (1)$$

$$2H^+ + 2e^- \rightarrow H_2 (E^0 = 0\ V) \quad (2)$$

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2 (E^0 = 1.23\ V) \quad (3)$$

To achieve such high endergonic photocatalysis process, a photocatalyst should require extra photon energy which can overcome the energy barrier of 1.23 eV. Hence, the photocatalyst possesses a band gap greater than 1.23 eV can initiate the photocatalysis process. In order toutilize the maximum portion of solar light, the band gap of photocatalyst must come in the visible region or band gap should be less than 3.0 eV.[12-13] Furthermore, a thermodynamically suitable photocatalyst for overall water splitting must have valence band maxima (VBM) more positive than water oxidation potential (O_2/H_2O (1.23 eV vs. NHE, pH=0) and conduction band minima (CBM) more negative than the water reduction potential of H^+/H_2 (0 eV vs. normal hydrogen electrode (NHE), pH=0) as shown in figure 1 (b). [12-13]

III. MXENE-BASED PLASMONIC HETEROSTRUCTURES

A. *Material Selection and Properties*

MXenes are described by the formula $M_{n+1}X_nT_x$, where surface terminations (-O, -OH and-F) significantly influence their properties. $Ti_3C_2T_x$ is particularly attractive due to its high electrical conductivity, hydrophilic nature, tunable electronic structure and strong optical absorption. Carbon-nitrogen based semiconductors such as **g-C_3N_4** and **C_2N** are good material due to their, visible-light activity, chemical stability and low cost and metal-free composition. **3.2 Plasmonic Enhancement Mechanisms**: This type of heterostructure enhances photocatalysis via following mechanisms:

- Hot carrier generation and injection: Plasmon decay produces energetic electrons that can transfer to the semiconductor conduction band.
- Near-field enhancement: Local electromagnetic fields increase photon absorption in the semiconductor.
- Improved charge separation: The molecule has intrinsic electric fields at the interface which is beneficial to reduce recombination process.
- Extended spectral response: Absorption can extends into visible-NIR regions. This absorption can be extends by surface termination engineering (T_x tuning) which will be used to monitor these effects.

IV. METHODOLOGY

In this section, we have discussed brief information of the basic fundamental theories and computational techniques which will require for completion of this work. As we know that every material is composed from the specific periodic arrangement of atoms in certain directions or paths. Hence, inherent properties and relative stability depends upon the atomic arrangements.

1) Relaxation Calculations:

First $Ti_3C_2T_x$ and C-N based semiconductors will relax separately then their heterostructure would be assembled and relaxed. All the ground state calculations will have been carried out using Vienna Ab initio Simulation Package (VASP)code to implement the projector augmented wave (PAW)method.The generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) exchange–correlation functional have been used for our system.[7-9] In some cases, GGA underestimate the calculated values such as band gap because of inadequacy of their exchange part of electronic self-interaction. Hence, slight mixing of Hatree-Fock with DFT gives better description of exchange-correlation.The DFT is unable to accurately describe long range interactions. Therefore, dispersion energy corrections are necessary for our calculations, hence we will include Grimme's D3-type[10] of semiempirical method for calculating the dispersion energy correction. For the understanding of chemical interaction (attraction and repulsion) among atoms in the materials, the charge density can be used. Therefore, we have used the algorithm developed by Henkelman group for the investigation of the Bader charges.[11]

2) TDDFT Calculations:

TDDFT calculations would be used orbital dependent GLLB-SC exchange-correlation functional which implemented in GPAW code employing the projector augmented-wave (PAW) method and double-ζ polarized (dzp) basis sets. The Wave functions would be denoted using a linear combination of atomic orbitals (LCAO).[12]

The optical properties will calculate using the LCAO-RT-TDDFT method as implemented in GPAW. And the optical spectrum would be computed using Delta pulse in specified direction.

Transition Contribution Map (TCM): The Transition Contribution Map (TCM) serves as a tool to visually represent the contributions of electron-hole transitions within the Kohn-Sham (KS) framework to the process of photoabsorption. In simple terms, the photoabsorption cross-section, denoted as S(ω), is formulated within the framework of occupied (i) and unoccupied (a) Kohn-Sham states, where S(ω) is represented as[13]

$$s(\omega) = \Sigma_{ia} S_{ia}(\omega) \quad (4)$$

matrix $S_{ia}(\omega)$ at specific resonance frequency are plotted in two-dimensional Gaussian-broadened plane where occupied and unoccupied KS states are shown by energy axes.

The colour employed in the map reflects the nature of the transition contribution such red for positive and blue for negative and the intensity of the colour conveys the contribution's magnitude. These maps are enriched with corresponding densities of states, and a diagonal line is included to denote the KS eigenvalue difference corresponding to ω.

3) Water Splitting Mechanism:

In this project, we will discuss the basic procedure of photo-electrochemical method of water splitting (i)The general photocatalysis process initiates by light irradiation followed by production of photoexcited charge carriers [electron (e^-) and hole (h^+)]; (ii) in second step, these charge carrier separate and migrate to the surface, simultaneously one competitive action also takes place which is bulk and surface recombination (photogenerated charge carriers recombines within a few nanoseconds which dissipates energy in the form of heat); (iii) in the last step, photogenerated e^- (h^+) reduce (oxidize) water which further produce hydrogen and oxygen, respectively. In thermodynamic point of view, complete water splitting is endergonic process with standard Gibbs free energy change (ΔG^0) +237 kJ/mol at 298 K temperature which is shown in equation (2-4):[1, 14]

$$H_2O \rightarrow \frac{1}{2O_2} + H_2 \; ; \Delta G^0 = 237 \frac{kJ}{mol} ; \Delta E^0 = 1.23 \; V \quad (5)$$

$$2H^+ + 2e^- \rightarrow H_2 (E^0 = 0 \; V) \quad (6)$$

$$H_2O \rightarrow \frac{1}{2O_2 + 2H^+} + 2e^- (E^0 = 1.23 \; V) \quad (7)$$

To achieve this overall reaction, a photocatalyst should require extra photon energy or band gap compared to 1.23 eV to initiate the reaction. The band gap of ideal catalyst should come in between 1.6-3.0 eV for utilizing maximum portion of solar light. Moreover, thermodynamic condition for suitable photocatalyst for overall water splitting must have valence band maxima (VBM) more positive than water oxidation potential (O_2/H_2O (1.23 eV vs. NHE, pH=0) and conduction band minima (CBM) more negative than the water reduction potential of H^+/H_2 (0 eV vs. normal hydrogen electrode (NHE), pH=0).

V. EXPECTED OUTCOMES AND IMPACT

Based on a comprehensive review of recent literature, MXene-based heterostructures have emerged as highly promising materials for efficient water splitting applications. Studies significantly show that integrating plasmonic components can improve the solar light absorption while also reduce the charge recombination process`. This synergistic effect plays a key role in lowering the overpotential required for the oxygen evolution reaction and in accelerating the kinetics of the hydrogen evolution reaction. Collectively, these findings help shape a clearer set of design principles for developing advanced plasmonic photocatalysts. Overall, the insights gathered from existing research point toward the strong potential of these systems in enabling more efficient, scalable, and cost-effective hydrogen production technologies.

VI. CHALLENGES

A. *MXene Oxidation and Stability*

MXenes, (e.g., $Ti_3C_2T_x$) are highly sensitive to oxidation, when exposed in aqueous or ambient environments, which leads to degradation of their electrical conductivity and loss of catalytic activity over time. This is due to primarily due to the presence of surface terminations (-O, -OH, and -F), which are reactive and can further facilitate oxidation. To minimize this issue, a controlledsurfacetermination is crucial. By tailoring the type and density of surface terminations, one can enhance resistance to oxidation (e.g., replacing –OH with more stable groups) which improves hydrophilicity and dispersion stability. Tuning electronic properties such as work function and conductivity, computational approaches (DFT-based studies) can help predict the most stable functional groups and their effect on electronic structure, suggests experimental strategies for long-term stability.

B. *Band Mismatch Issues:*

Another issue is the band mismatch of MXene-based heterostructures which hindered the internal energy transfer. Moreover, improper alignment of the conduction band minimum (CBM) and valence band maximum (VBM) can result in poor separation of photogenerated electron-hole pairs, increased recombination rate and reduced photocatalytic efficiency.

To overcome this, systematic screening of semiconductors (such as g-C_3N_4, MoS_2, CdS, etc.) is essential. One can do the high-throughput computational screening and design a machine learning models which significantly accelerate the identification of optimal semiconductor material with favourable band alignment and charge transfer characteristics.

C. *Interface Instability*

Third concerned issue is thestability of interface between the MXene and the semiconductor. Weak interfacial interaction can degrade the structural degradation, poor charge transfer across the interface and reduced durability under operating conditions.

To address this issue, we need to observe bindingenergies to ensure strong interactions between two layers.

VII. CONCLUSION

This review mainly focussed on the comprehensive computational framework for the various design of MXene-based plasmonic heterostructures to enhance photocatalytic water splitting performance. By incorporating the advanced electronic structure calculations with detailed plasmonic analysis, the work systematically addresses key challenges such as charge separation, light absorption, and interfacial charge transfer mechanism. Here such study is based on the understanding the role of MXenes (e.g., $Ti_3C_2T_x$) as both conductive platforms and plasmonic booster when coupled with appropriate semiconductor materials.

Such framework not only enables the prediction of accurate band alignment and interface stability but also provides chemical insights into plasmon-induced hot carrier generation and transfer mechanisms. These findings show clear structure-property relationships that can focus light on the targeted design of efficient and stable photocatalytic systems.

Overall, this work offers both fundamental understanding and practical design principles for next-generation photocatalysts. The proposed approach is expected to accelerate the development of high-performance, durable materials for solar-driven hydrogen production, thereby contributing meaningfully to the advancement of sustainable and clean energy technologies.

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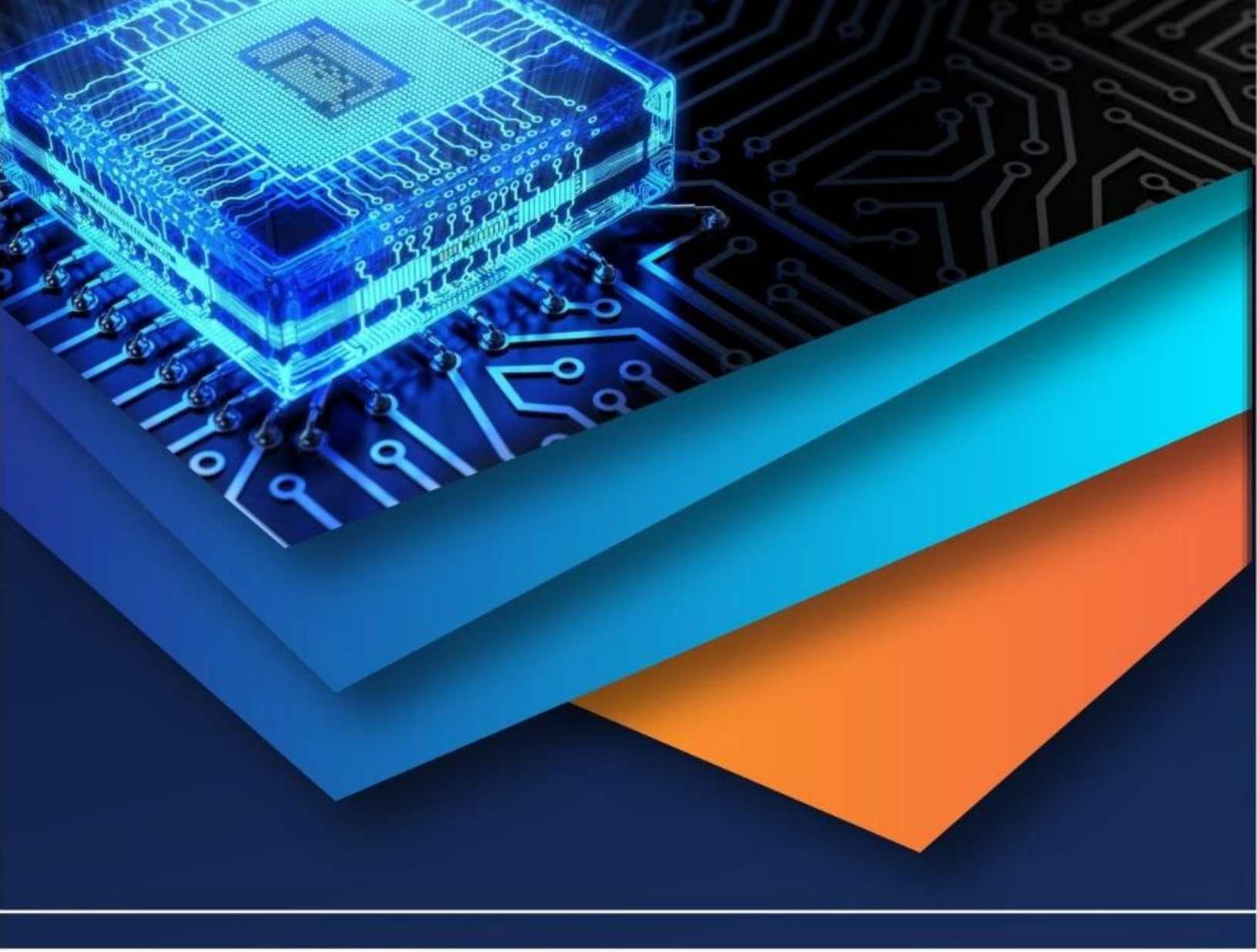

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