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## 2D Materials as Thin Films: Graphene and Beyond

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**Abstract:** The paper discusses the exceptional characteristics and vast usage regarding 2D materials, focusing on advancements other than the widely researched graphene. It studies various 2D materials, like metal oxides, transition metal dichalcogenides, and metal-organic frameworks, which exhibit different electronic and structural properties than graphene [1], [2]. The review outlines the different synthesis methodologies used to obtain few-layer, single-layer, and multilayer assemblies of these materials, in solution and on different substrates, also at wafer scales [3]. This involves the observation of developments in the large-area synthesis technologies which are essential in the process of industrial scalability [4]. Moreover, the article explores the importance of the advanced characterization designs in explaining the atomic structure, electronic band properties and quantum phenomena of these emergent 2D systems [5], [6]. This level of understanding is important in exploiting their distinct electrical, optical, chemical and thermal characteristics in next generation technological uses [7]. The isolation of graphene in 2004 was a turning point and sparked the emergence of the research on 2D materials [8]. This resulting in discovering different novel 2D materials, such as black phosphorus, transition metal dichalcogenides, MXenes, and hexagonal boron nitride which all have a different quantum-confined energy band structure because of the in-plane lattice periodicity [9]. The expansion of 2D materials has now gone beyond this to include even wider range of compositions, such as metal oxides, phosphides, and other layered perovskites, and further diversification of their potential applications [10], [11]. This fast-moving era has led 2D materials to develop into a sub-discipline of physical sciences with numerous applications [12].

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### 1. Introduction

In 2004, graphene was extracted from graphite and triggered a great deal of attention in 2D materials for their unique characteristics and applications [13]. This pioneering work triggered the combinatorial investigation of other van der Waals (vdW) materials with break-even exfoliation for various few-layered and single-layered structures other than graphene being achieved: black phosphorus, hexagonal boron nitride, transition metal dichalcogenides, also many metal oxides [14]. They are materials with good in-plane covalent bonding with weaker out-of-plane vdW bonding, forming a distinct set of optical, electronic, mechanical and thermal properties that are not to be confused with their bulk behavior, which can be explained in large part by the effects of quantum confinement [15], [16]. Their unique properties of electrical and thermal conductivities, mechanical strength are surpassing the limits of traditional material physics and promising exciting applications in flexible electronics, advanced composites and quantum devices [17], [18]. After the discovery of graphene, there has been different 2D materials such as hexagonal

boron nitride, transition metal dichalcogenides and MXenes with intriguing quantum properties [19].

It is an expansion of phosphorene and other elemental 2D materials, which continue to diversify the 2D systems landscape [20]. Of these, one of the rising-star 2D materials has been black phosphorus, which has overcome the bandgap constraints of the zero-gap 2D material graphene but retains a relatively large bandgap, comparable to the transition metal dichalcogenides (MoS<sub>2</sub> and WSe<sub>2</sub>) [21], [22]. This growth has resulted in the creation of improved synthesis strategies with the achievement of materials like hexagonal boron nitride, silicene, metalorganic frameworks, black phosphorus, covalent organic frameworks, MBenes and MXenes [23]. This ongoing finding and definition of new 2D materials highlights the fast pace at which this area is evolving beyond simple monolayers to complex heterostructures with new emergent properties not reflected in individual constituent materials [24].

### Literature Review

The study of 2D materials has gone beyond the individual monolayers into 2D heterostructures, whereby novel properties can be achieved through the controlled vertical stacking or lateral stitching of the various single layers [25]. These heterostructures can be used to achieve vdW-based electronic band alignments and quantum phenomena, and provide the ability to create customized functionalities that are not available in the underlying monolayers [26]. An example is the blue phosphorene when used in combination with the transition metal dichalcogenides, like MoSe<sub>2</sub> and MoS<sub>2</sub>, showing a potential of effective thin-film solar cells as well as optoelectronic devices with energy conversion efficiency demonstrating a potential of 1.16% and 0.98% respectively [27].

Such flexibility in material combination provides a wide range of tunability of electronic, thermal, and optical properties of various 2D materials, such as graphene, black phosphorus, transition metal dichalcogenides, and MXenes [28], [29]. In addition to these, many other 2D materials, including phosphorene and hexagonal boron nitride (hBN), were discovered, expanding the material library to a variety of applications [30], [31]. Such 2D heterostructures have important benefits over traditional heterojunctions, such as the ability to control the thickness of each vertical layer atomically, the ability to create perfect interfaces without requiring buffer layers to overcome lattice mismatch and the ability to study interlayer coupling to design more advanced optoelectronic devices [32]. The 2D/2D heterojunctions, their strategic design, and their use are specifically useful in catalytic applications, with high surface-area-to-volume ratios, allowing various active sites, and with optimal charge transfer pathways due to their ultrathin nature and optical transparency useful in light absorption in photocatalysis [33].

## 2. Material and methods

This has prompted a focus on the characterization and the synthesis of materials towards the assembly of van der Waals heterostructures (vdWHs) based on the stacking of different 2D materials, enabling the tuning of the electronic properties, the photocatalytic activity and the optoelectronic responses [34], [35]. This strategy can be used to design crystal structures with tunable optical and electronic properties to surpass the limitations of the individual 2D monolayers, such as the absence of band gap in graphene [36]. The heterostructures can be engineered to realize particular band structures and charge transfer processes, which is essential for the operation of devices in optoelectronics, photovoltaics and catalysis [37].

For example, researchers use density functional theory to predict, design and realize bandgaps and structures in such 2D vdWHs to achieve specific functions by incorporating materials such as graphene, hexagonal boron nitride and transition metal dichalcogenides [38]. This type of stacking also allows the discovery of new phenomena at the interfaces

with this strategic placement, along with the interaction of the components in the structure to yield new properties that are essential in achieving more efficient energy-conversion systems [39]. The delicate control of the stacking sequence and interlayer interactions and the layer thickness of such vdW heterostructures result in exotic carrier dynamics and therefore enable the broad-band optoelectronics, high-frequency electronics and low-power neuromorphic computing [40]. This computer-driven design and stacking of diverse 2D materials to form heterostructures leads to the formation of designer crystal lattices with tunable electronic and optical properties, similar to molecular beam epitaxy [41].

### 3. Results

Such rational design of 2D nanocomposites that have hybrid structures permits the design of multi-functional materials with customized properties, such as increased catalytic activity through improved surface properties and electron transfer pathways [42]. In particular, this includes utilizing the exceptional properties regarding 2D materials, like their high surface-to-volume ratio which gives them an extensive number of active sites and their ultrathin structure which reduces the paths of charge carrier migration [43]. These properties can be further optimized by purposeful design of vdWHs that enable a fine control of the alignment of the bands and enables easy separation and transfer of charges, which is paramount to increased photocatalytic activity [44], [45], [46]. As an illustration, the local electron density can be reconfigured in heterostructures by a strategic combination of 2D materials, which results in unpaired orbital electrons, which enhance the surface catalytic reaction by making the adsorption and desorption of molecules easier [47].

Such a cautious architectural design enables the formation regarding highly efficient photocatalysts with high light absorption as well as low recombination rates of charges [48]. The formation regarding 2D/2D heterojunctions could eliminate or reduce Schottky barrier because of weak Fermi-level pinning, considerably enhancing the efficiency of charge transfer at the interface [49]. In addition, these heterostructures could have an increased photoelectrocatalytic activity because the strong interaction between light and matter, high quality charge transport, and chemically stable nanosized structures [50]. This is an exact synthesis of 2D/2D heterojunctions which takes advantage of the close point of contact and strong interfacial charge transfer to achieve the highest catalytic performance and the highest energy conversion efficiencies in various applications [51]. These 2D-2D hybrid materials are highly developed materials, especially metal chalcogenides, which have shown great promise in energy conversion and energy storage because of their exceptional photo- and electrochemical properties [52].

### 4. Discussion

Their electronic structure and surface chemistry could be precisely controlled through fabricating these materials at the atomic scale, which in turn enables tailoring the properties of these materials to particular catalytic reactions [53]. To give an example, the establishment of heterojunctions in between various 2D materials can produce intrinsic electric fields at the interface, which greatly increases charge separation and transport, which play a paramount role in improving catalytic efficiency [54]. The benefit of this synergy (typically vdW interactions) is charge redistribution, enhanced reaction rate and band gap tuning, which in turn enhances structural stability and charge transfer rate [55]. These 2D/2D heterojunctions are also known to have high surface areas, which is important to promote high heterojunction effects, important for catalysis [56].

These systems tend to be stable as well as have better coupling at the heterointerfaces than other 2D/low-dimensional heterojunctions, enabling photoinduced charge transfer

and separation [57]. The alignments of type-II bands created by this strategic stacking of various 2D materials allow the separation of charges carriers and prevent recombination, thus boosting photocatalytic activity [58], [59]. Moreover, rational choice and incorporation of various 2D nanomaterials in heterostructures characterized by strong interfacial interactions is also a promising approach to the creation of new artificial photocatalytic materials with improved performance due to the extension of their performances and control of their multiple interfaces [60].

## 5. Conclusion

Finally, the extraordinary characteristics of 2D materials, especially when used in vdWHs, are a paradigm shift in the high-performance materials. These heterostructures have very high benefits since they have a high interfaces surface area which facilitates fast charge transport and complementary effects between elements that enhance conductivity and improvement of electron/ion transfer channels [61]. The accurate control of the electronic structure, and surface chemistry made possible by such integration enables high tunable catalytic properties, which result in high efficiencies in many different energy conversion and storage applications [62], [63].

The flexibility of band alignments and high interlayer coupling of 2D/2D vdWHs allows optimized electron interactions, which will be important to enhance photocatalytic activity, particularly in applications where efficient electron-hole separation is necessary [64], [65]. Moreover, charge carriers can be physically segregated by engineering of appropriate interfacial domains in these heterostructures and their lifetimes can be longer, despite a decrease in the potential energy of photoexcited electrons, as is observed in CN/h-BN systems [66]. This has been especially observed in type-II heterostructures, in which the staggered band alignment spatially isolates photogenerated electrons and holes into different layers, which effectively inhibits recombination and greatly enhances photocatalytic activity [67], [68], [69]. The real space separation of charge carriers is a key factor in the enhancement of the efficiency of every type of photocatalytic reaction, including the water splitting [70].

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