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Tuning Interfacial Chemistry with Twistronics

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Abstract

Moiré superlattices have introduced a new degree of freedom, interlayer twist, for tuning electronic and optoelectronic behavior of two-dimensional materials. A periodically modulated crystallographic registry, controlled by twist angle, manifests localized electronic states and modifies interlayer coupling. Advances in two-dimensional catalysts present twisted materials as a platform for manipulating interfacial chemistry.

Keywords:

moiré superlattices, twistronics, electrocatalysis, photocatalysis

Twistronics for interfacial chemistry

Artificial van der Waals (vdW) heterostructures, constructed by stacking atomically thin two-dimensional (2D) layers, are a distinctive platform for tailoring interfacial chemical transformations [1]. The reduced dimensionality renders the materials a considerable surface-to-volume ratio coupled with exceptional tunability of their physicochemical properties. Additionally, vdW heterostructures possess weak interlayer interactions that allow modification of the crystallographic registry between layers via manipulation of the interlayer twist angle, introducing another degree of freedom for material engineering. Stacking 2D layers with controlled interlayer rotations generates an in-plane quasiperiodic modulation of crystallographic registry, represented as a moiré superlattice (Figure 1A,E). This periodically modulated structure manifests a ubiquitous twist angle-dependent interlayer coupling, giving rise to tunable electronic and optoelectronic properties that can be leveraged to bring about desired chemical activities [2].

The field of “twistronics” emerged with the discovery of a variety of exotic physical phenomena in twisted graphene and transition metal dichalcogenides (TMDs) [2]. Apart from attracting a surge of interest in quantum physics, moiré constructs are also a distinctive paradigm for systematically manipulating interfacial chemical transformations, opening new avenues for application of vdW materials in catalysis and energy conversion. Specifically, twistronics have been used to regulate (i) electron transport within the material or across a solid-liquid interface; (ii) free energy associated with stabilizing or destabilizing intermediates in a catalytic cycle; and (iii) light absorption and photogenerated carrier dynamics.

¹ Deng, D. *et al.* (2016) Catalysis with two-dimensional materials and their heterostructures. *Nat. Nanotechnol.* 11, 218-230.

² He, F. *et al.* (2021) Moiré Patterns in 2D Materials: A Review. *ACS Nano* 15, 5944–5958.

Tuning charge transfer

Efficient electrochemical processes require rapid electron transport across solid–liquid interfaces. The basal plane of many vdW materials is considered an electrochemically inert surface due its minimal electronic density of states (DOS). However, recent work has shown that the basal plane of graphene bilayers can be activated by controlling the interlayer twist angle to generate non-dispersive (flat) electronic bands in the system (Figure 1B,C,F) [3]. These flat bands, created at a “magic angle” of $\sim 1.1^\circ$ for twisted bilayer graphene (tBG), exhibit a massively enhanced DOS (Figure 1D) that governs interfacial electron transfer kinetics, as demonstrated for the outer-sphere electroreduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ (Figure 2A). The energy levels at which an enhanced DOS appear, called van Hove singularities (vHS), are determined by the twist angle, sparking the possibility of also manipulating interfacial photochemistry via hot electron transitions outside of the “magic angle” regime. Resonance between incident light and vHSs has been exploited to promote photogeneration of energetic electrons for surface functionalization of tBG [4].

Although the basal plane of semiconducting TMDs can be activated by introducing vacancies, doping, or inducing phase transitions, the electrochemical performance of these materials is often limited by weak interlayer charge transport [5]. The interlayer potential barrier in MoS_2 can be reduced by using a twisted interface to tune interlayer coupling, thus promoting

³ Yu, Y. *et al.* (2021) Tunable electrochemistry with moiré flat bands and topological defects at twisted bilayer graphene. arXiv:2108.06826

⁴ Liao, L. *et al.* (2015) van Hove Singularity Enhanced Photochemical Reactivity of Twisted Bilayer Graphene. *Nano Lett.* 15, 5585-5589.

⁵ Jiang, Z. *et al.* (2019) MoS_2 Moiré Superlattice for Hydrogen Evolution Reaction. *ACS Energy Lett.* 4, 2830-2835.

electron transfer from a conductive substrate to active sites in the TMD layers. With this approach, twisted bilayer MoS₂ moiré superlattices, in the form of nanoscrolls, exhibited an improvement in catalytic performance for the hydrogen evolution reaction (HER) compared to untwisted bilayers [5].

Regulating intrinsic catalytic activity

Electrocatalytic reactions are generally multi-step processes involving complex adsorption and desorption of the reactants, intermediates, and products. The reaction kinetics is largely determined by the Gibbs free energy associated with adsorption of key intermediates. For HER, the Gibbs free energy of hydrogen adsorption (ΔG_{H}) is a quantitative descriptor of the intrinsic activity [6]. TMDs have shown immense potential as HER catalysts since their ΔG_{H} is readily tuned, often via defect and strain engineering. Both experimental [7] and computational [6] studies have drawn compelling correlations between ΔG_{H} and the interlayer electronic coupling tuned by moiré architectures, indicating that the intrinsic HER activity of TMDs can also be controlled using twistrionics.

Experimentally, moiré structures in WS₂ nanobelts resulted in a lower overpotential for HER compared with non-twisted WS₂ [7]. This enhancement originates from modulation of the electronic structure in TMD active sites due to the moiré pattern, which shifts the W *d* bands and S *p* bands upward, leading to a more favorable ΔG_{H} [7]. Density functional theory calculations have also revealed that XX stacking regions in twisted NbS₂ moiré superlattices (where chalcogen atoms are locally aligned) have a favorable ΔG_{H} of 0.01 eV, whereas HER is

⁶ Zhang, Y. *et al.* (2021). Moiré metal for catalysis. arXiv:2111.03058

⁷ Xie, L. *et al.* (2021) WS₂ moiré superlattices derived from mechanical flexibility for hydrogen evolution reaction. *Nat. Commun.* 12, 5070.

thermodynamically inaccessible in the NbS₂ system without twisting [6]. In fact, bilayer NbS₂ with a twist angle of 5.08° is predicted to lie near the peak of the HER volcano plot (Figure 2B), indicating it should be a superior HER catalyst with an intrinsic activity exceeding that of all currently known materials.

Tuning light absorption and hot carrier excitation

Beyond surface reactivity, the efficiency of photocatalytic reactions depends on light absorption and the dynamics of photogenerated carriers. Accordingly, the photocatalytic behavior of vdW materials can be tuned by using twistrionics for bandgap engineering and manipulation of hot carrier dynamics. The synthesis of bismuth oxychloride (BiOCl) moiré superlattices has been realized in bottom-up chemical growth of spiral nanosheets [8]. The head-to-head arrangement of Cl atoms in AA-stacked regions of the BiOCl moiré results in the emergence of a distinct valence band (Figure 2C), leading to a smaller band gap and localization of photogenerated holes. As a result, twisted BiOCl showed remarkably improved performance for photocatalytic degradation of Rhodamine B, stemming from the enhanced visible light absorption, more efficient charge separation, and increased carrier lifetime.

In another study, first-principles and *ab initio* molecular dynamics calculations predicted superior photocatalytic water splitting activity in twisted graphitic carbon nitride (g-C₃N₄) bilayers [9]. Similar to the previous example, the moiré pattern in twisted g-C₃N₄ induces spatial

⁸ Liu, L. *et al.* (2019) Bottom-up growth of homogeneous Moiré superlattices in bismuth oxychloride spiral nanosheets. *Nat. Commun.* 10, 4472.

⁹ Zhang, X. *et al.* (2021) Ultrafast Interlayer Charge Separation, Enhanced Visible-Light Absorption, and Tunable Overpotential in Twisted Graphitic Carbon Nitride Bilayers for Water Splitting. *Adv. Mater.* 33, 2104695.

localization of the valence and conduction bands combined with a band gap reduction due to broken symmetry. In addition to the optoelectronic properties tailored for photocatalysis, twisted g-C₃N₄ moiré structures also possess localized valence bands orbitals that regulate the overpotentials for hydrogen and oxygen evolution reactions.

Concluding remarks and future perspectives

Twisted vdW architectures exhibit distinctive electronic and optoelectronic properties that establish an extraordinary platform for manipulating interfacial chemical transformations. Remarkably, thermodynamically unfavorable crystallographic registries become accessible in moiré structures (*e.g.* AA stacking in twisted graphene), producing localized electronic states [3,6,8,9] and long-range modulation of interlayer coupling [5,7,8]. While a handful of pioneering work has demonstrated the feasibility of exploiting these characteristics to tune interfacial chemistry, the scope and versatility of this field still have significant room for extension in new directions.

Formulating strategies to control interlayer rotation in the vast collection of other vdW materials will extend the application of moiré chemistry beyond graphene and common TMDs. We anticipate that rigorous preparation of well-defined twisted moiré surfaces with controlled twist angles, especially in “magic angle” regimes, will shed light on the role of moiré flat bands in regulating the adsorption energy of catalytic intermediates. We also suggest that high resolution electrochemical mapping via scanning probe techniques will illuminate correlations between surface activity and structural domains defined by moiré patterns.

The fundamental band structure reconfiguration in twisted vdW layers may also be leveraged in combination with orthogonal tuning knobs to control interfacial chemistry.

Electrostatic gating [¹⁰] alters the carrier concentration in conventional solid-state devices as well as electric double-layer transistors, allowing independent control over the electronic bands in moiré structures. Additionally, the intercalation of guest species into the gaps between twisted vdW layers offers opportunities for investigating the interplay among intercalants, host lattices, and chemical activity. Coupled with moiré quantum engineering, we envision that the intercalants may localize at specific atomic registries [¹¹], providing an additional spatial control over interfacial chemistry.

¹⁰ Wang, Y. *et al.* (2019) Field Effect Modulation of Electrocatalytic Hydrogen Evolution at Back-Gated Two-Dimensional MoS₂ Electrodes. *Nano Lett.* 19, 6118-6123.

¹¹ Zou, Y.-C. *et al.* (2021) Ion exchange in atomically thin clays and micas. *Nat. Mater.* 20, 1677-1682.

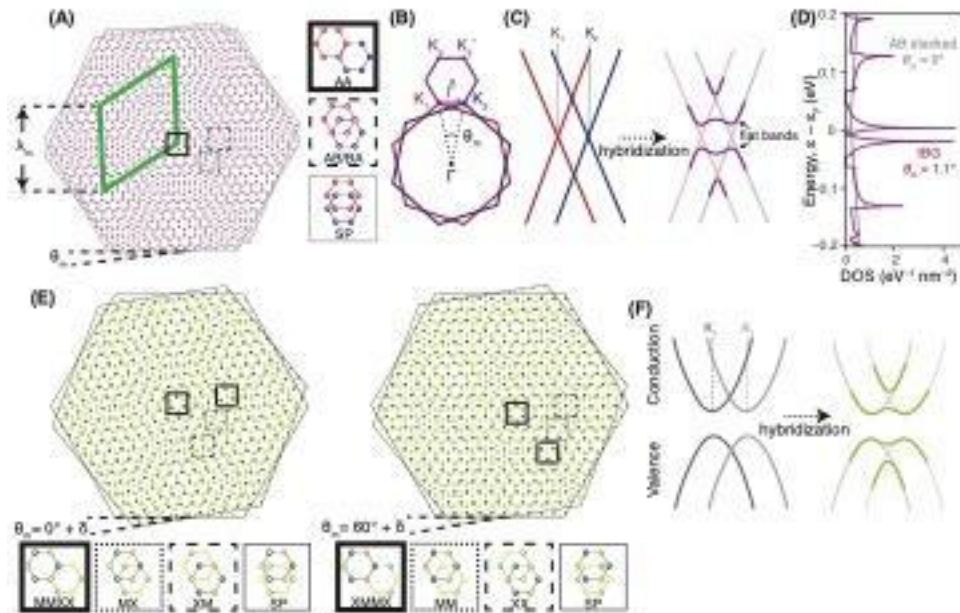


Figure 1. Flat band formation in moiré superlattices. (A) Schematic of moiré pattern formed in twisted bilayer graphene (tBG), with three high-symmetry stacking configurations highlighted. (B) The mini-Brillouin zone of a tBG superlattice formed by the difference between graphene wavevectors K_1 (layer 1) and K_2 (layer 2). (C) Illustration of band hybridization in tBG, producing flat bands. (D) Calculated DOS for 1.1° tBG. (E) Schematic of moiré patterns for parallel (left) and anti-parallel (right) stacking configurations of twisted transition metal dichalcogenides (TMDs), with high-symmetry stacking sequences highlighted. (F) Illustration of band hybridization and flat bands in twisted TMDs. Panel D adapted, with permission, from [3].

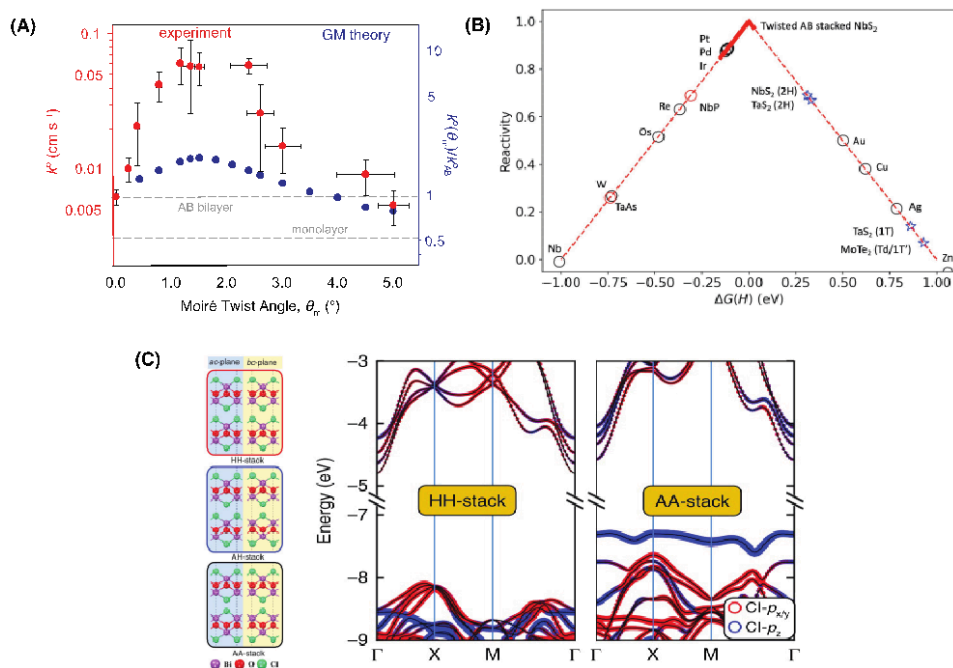


Figure 2. Interfacial chemistry tuned by moiré superlattices in twisted van der Waals catalysts. (A) Standard rate constants (k^0) of $\text{Ru}(\text{NH}_3)_6^{3-}$ electroreduction at twisted bilayer graphene as a function of twist angle, θ_m . (B) Predicted hydrogen evolution reaction (HER) reactivity following the volcanic scheme as a function of calculated Gibbs free energy of hydrogen absorption, ΔG_H . (C) BiOCl bilayer structures with different stacking sequences (left) and distinct band structures of the HH-stack and AA-stacking configurations (right). Panel (A) adapted, with permission, from [3]. Panel (B) adapted, with permission, from [6]. Panel (C) adapted, with permission, from [8].

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Declaration of interests

No interests are declared.

Reference