Transition Metal Chalcogenide Single Layers as an Active Platform for Single-Atom Catalysis

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ABSTRACT: Among the main appeals of single-atom catalysts are the ultimate efficiency of material utilization and the well-defined nature of the active sites, holding the promise of rational catalyst design. A major challenge is the stable decoration of various substrates with a high density of individually dispersed and uniformly active monatomic sites. Transition metal chalcogenides (TMCs) are broadly investigated catalysts, limited by the relative inertness of their pristine basal plane. We propose that TMC single layers modified by substitutional heteroatoms can harvest the synergistic benefits of stably anchored single-atom catalysts and activated TMC basal planes. These solid-solution TMC catalysts offer advantages such as simple and versatile synthesis, unmatched active site density, and a stable and well-defined single-atom active site chemical environment. The unique features of heteroatom-doped two-dimensional TMC crystals at the origin of their catalytic activity are discussed through the examples of various TMC single layers doped with individual oxygen heteroatoms.

Single-atom catalysts (SACs) have recently shifted into the focus of heterogeneous catalysis research. The size reduction of the catalytic particles from macro-, to nano-, and finally atomic scale progressively increases the number of under-coordinated atoms and raises the surface free energy. This leads to increasing the site reactivity and therefore strengthening interaction with the support and adsorbates. In the ultimate limit of single-atom catalysts, the surface free energy is maximal, leading to unique chemical properties of the system. Most often group 8 metal atoms are investigated as promising SACs that ideally reside as individually dispersed metal atoms on a solid surface. The main hurdle to overcome for realizing efficient SACs is the relatively low density of the active sites, as increasing the site density results in the aggregation of the individual atoms into larger clusters and nanostructures, driven by their surface energy. To avoid this, a stable anchoring (strong bonding) of individual heteroatoms at well-defined sites on solid surfaces is required.

In particular, it was recently demonstrated that graphitic carbon nitride supporting Pd or Pt SAC exhibits excellent activity in CO₂ reduction during photocatalytic conversion. It has also been shown that silver chains embedded in manganese oxide showed excellent activity for the HCHO oxidation. Individual Rh atoms located on CoO substrates demonstrated remarkable activity and selectivity toward propene hydroformylation. A facile one-step method was recently shown to yield well-dispersed Ru atoms on the top of the iron atoms in mono-NiFe displaying a high activity for the hydrazine electrooxidation. Catalysts consisting of individual Pt atoms anchored to the iron oxide surface demonstrated excellent stability and high activity for CO oxidation. Nitrogen-coordinated transition metal-doped carbon materials were shown to comprise homogeneously dispersed single M–N₅ sites that efficiently catalyze the electrochemical reduction of CO₂.

However, the activity of SACs is still restricted by the modest active site density and limited stability that can be achieved, both stemming from the relatively weak binding to...
the substrate. Here we propose to achieve a stable high-density dispersion of heteroatoms by incorporating them individually into the crystal structure of TMC single layers. This approach relies on the susceptibility of TMCs for chalcogenide atom exchange, which makes them a good candidate for hosting substitutional heteroatoms. However, TMCs not only are a promising support but also can catalyze various reactions on their own, such as hydrogen evolution or hydrodesulfurization. Traditionally, the edges of TMCs are regarded as catalytically active, while the activity of the basal plane is generally low in the pristine form. The single-layer form of bulk TMC catalysts have recently become the subject of investigations for catalytic applications as their electronic structure can substantially differ from that of the bulk. In contrast to the indirect band gap bulk TMC crystals, single layers are often direct band gap semiconductors, enabling a stronger interaction with light and more efficient photocatalytic applications. MoS2 single layers were shown to display higher catalytic activity than their bulk crystals, which can be attributed to the modified electronic structure, as well as a reduced pathway of the charge carriers to accessible active sites on the surface. Manipulating the basal plane of two-dimensional (2D) TMC crystals holds the promise of substantially increasing their catalytic activity. Introducing defects into their basal plane structure is a viable option to achieve this goal. Sulfur atom vacancies in MoS2 monolayers have been shown to act as catalytically active centers. However, the dangling bonds of such unsaturated vacancies are energetically unfavorable, which is expected to lead to their rapid saturation.

A related but more stable defect type is when single heteroatoms substitute host crystal atoms that is, vacancies are occupied by heteroatoms. If catalytically active, this defect type provides a stable, well-defined structure with strongly bound atoms, which is highly appealing for SAC. It has been indeed shown that Co atoms covalently attached to S vacancies in MoS2 single layers efficiently catalyze the hydrodeoxygenation reaction. Furthermore, even though not directly accessible on the surface, Pt atoms replacing Mo atoms of MoS2 crystals have been shown to enhance the catalytic activity. We have recently demonstrated that single-oxygen-atom dopants incorporated into the 2D MoS2 crystal structure substantially enhance the catalytic activity of MoS2 single layers for the hydrogen evolution reaction. Furthermore, such O atom substitution sites displayed a good catalytic and structural stability over several catalytic cycles. Similar nonmetal atoms have been also shown to act as SACs in graphene for the oxygen reduction reaction. These findings can open the way toward developing inexpensive nonmetal SACs by using 2D materials as their active substrate.

In this Perspective, we discuss the possibility that 2D TMC crystals substitutionally doped with individual heteroatoms can be highly efficient electrocatalysts because of the combined effect of the SAC and the activation of the basal plane atoms near the defect sites. We propose that 2D TMCs can provide a highly versatile platform to realize high-density single heteroatom sites and discuss how such substituted structures can enhance the catalytic activity.

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**Easy and Versatile Preparation.** Synthesizing individually dispersed atoms on solid substrates is one of the key challenges in single-atom catalysis. Various synthesis methods have been proposed, including photochemical methods, atomic layer deposition, or the pyrolysis of metal–organic frameworks. However, even today, the relatively low site density that can be achieved is a major restriction for the activity of single-atom catalysts. Therefore, novel and more efficient synthesis methods are highly desirable. In the case of SACs, a stable anchoring of individual heteroatoms to the substrate is required to prevent their aggregation. We propose that this can be realized through substituting single atoms of the TMC basal plane with the desired heteroatoms. In the case of TMC crystals, this is facilitated by their susceptibility for chalcogenide atom exchange, making them a good candidate for hosting substitutional single heteroatoms. This approach resembles the case of single-atom alloy catalysts formed by individual metal atoms with a different metal substrate.

We briefly outline three strategies to synthesize heteroatom-doped 2D TMC crystals. Introducing dopant atoms during the synthesis of TMD single layers is a straightforward approach. The chemical vapor deposition (CVD) growth of MoS2(1−x)Sex crystals has been demonstrated, where the S/Se ratio can be continuously tuned. However, the individual dispersion of dopants for higher concentrations has yet to be verified. Nitrogen- and phosphorus-doped MoS2 layers have also been grown and displayed enhanced catalytic activity for hydrogen evolution and oxygen reduction reactions, respectively. A second approach is the post synthesis modification by creating chalcogenide atom vacancies and saturating them with the desired heteroatoms subsequently. TMC single layers are characterized by a relatively high concentration of native vacancies, and their concentration can be further increased by annealing at high temperatures, electrochemical reduction, or plasma treatment. This route has been followed when attaching individual Co atoms to MoS2 single layers for realizing Co SACs for the hydrodeoxygenation reaction. A similar post synthesis approach involves the exchange of individual chalcogenide atoms to heteroatoms through chemical substitution reactions. This has been demonstrated for the O substitution reaction of MoS2 under ambient conditions, as well as the Te substitution of S atoms, transforming MoS2 into MoTe2.

The synthesis methods outlined above are expected to provide relatively simple and efficient preparation techniques for single heteroatom centers substitutionally incorporated and individually dispersed on 2D TMC substrates, exploiting the affinity of TMC crystals toward chalcogenide atom exchange.

**High Active Site Density.** Besides versatile synthesis methods, TMC single-layer substrates with embedded heteroatoms also offer the benefit of site densities that are much higher than those reported previously in the literature for metal SACs on various substrates.

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scanning tunneling microscopy. Figure 1 shows two examples of resolving the individual heteroatom (oxygen) sites embedded into MoS$_2$ and WS$_2$ single layers by scanning tunneling microscopy. The samples have been prepared by annealing the exfoliated single layers at 130 °C in air for a week. While in this case the heteroatom site densities are of the order of 10$^{13}$ cm$^{-2}$, it can be easily increased into the range of 10$^{14}$ cm$^{-2}$, corresponding to about 10% of the sulfur atoms of the top layer. These values are clearly superior to previously achieved site densities, although in the majority of SACs, the site densities cannot be precisely determined. The ability to directly image the structure of catalysts at the single atom level is particularly important, not only for the accurate determination of the site density but also for providing unmatched structural information on the embedded single sites and their atomic environment.

Single-Site Catalysts. While single heteroatoms are all equivalent, their bonding to the substrate may occur in various configurations. A good example is graphene doped by N atoms, where the dopant structure can acquire several distinct atomic configurations, such as pyridinic, pyrrolic, and graphitic, and it is challenging to prepare samples with a single type of N bonding.20

According to our density functional theory (DFT) calculations for the investigated TMC single layers (2H−: MoS$_2$, MoSe$_2$, MoTe$_2$, WS$_2$, WSe$_2$, WTe$_2$), substitutional O heteroatoms strongly prefer a single bonding configuration (above the center of the triangle formed by the three underlying Mo atoms). To confirm this, we performed detailed calculations for various binding configurations of the O atom into the chalcogenide vacancy. The lowest energy was always found for the O atom positioned at the center of the three underlying metal atoms with equal distances from each of them. Deviation from this symmetrical configuration significantly increased the total energy of the system and provided no stable configuration. Consequently, the substitutional doping sites in TMC basal planes enable the realization of single-site heterogeneous catalysts with many identical, catalytically active sites dispersed on the crystal surface. Such single-site catalysts can provide an ideal model system enabling the systematic understanding of the structure−activity relationship at the atomic scale. This feature is commensurable to that of the model catalysts like single crystal, from the perspective of capturing the essential features of a working catalyst.34−36

In the following we will discuss the potential mechanisms responsible for the catalytic activity of heteroatoms incorporated by substitution in various TMC crystal structures through investigating the role of oxygen heteroatoms in catalyzing the hydrogen evolution reaction.

Decreasing H Adsorption Potential on Heteroatom Sites. Heteroatom substitutions can induce defect states inside the band gap. These electronic states were proposed to increase the catalytic activity through facilitating the H atom adsorption.15 However, for isoelectronic heteroatom substitutions, such as oxygen in TMCs, defect states are absent from the gap. Consequently, their influence on the adsorption and
catalytic activity is expected to be lower. Nevertheless, we have demonstrated for O-doped MoS\textsubscript{2} single layers that even isoelectronic heteroatoms can substantially increase the catalytic activity. A widely used descriptor for the catalytic activity is the H atom adsorption Gibbs free energy $\Delta G_{\text{H}}$ which should not be too high (unfavorable adsorption) or too low (unfavorable desorption) in an efficient catalyst. In the case of TMC single layers, $\Delta G_{\text{H}}$ was calculated to be around $-2.5$ eV, which indicates a highly unfavorable adsorption to the pristine basal plane. To understand the role of O atom sites in the catalysis, we have also calculated the $\Delta G_{\text{H}}$ values at the O atom substitution sites in various TMC crystals. Figure 2a provides evidence that the H atom adsorption free energy considerably decreases, indicating a more favorable H atom adsorption on O substitution sites than the pristine S atom sites of the basal plane. Our calculations predict that in Mo-based TMC single layers the gain in the adsorption potential achieved by O-substitution is higher than for W-based TMCs. Although lowering the adsorption potential at heteroatom sites is a significant effect, it is not strong enough to account for the activation of the catalytic process alone, as $\Delta G_{\text{H}}$ values around 1 eV still indicate a relatively low adsorption probability.

**Charged Heteroatom Sites.** The strong bonding of heteroatoms to the substrate required to achieve their stable anchoring implies an enhanced interaction with the substrate that in turn facilitates an efficient charge transfer. Substitution of heteroatoms with different electronegativity as compared to the substituted chalcogenide atoms induces a local redistribution of the charge density. This can create a complex charge density landscape where ions can find their preferred sites for efficient adsorption and charge transfer.

Substitution of heteroatoms with different electronegativity as compared to the substituted chalcogenide atoms induces a local redistribution of the charge density. This can create a complex charge density landscape where ions can find their preferred sites for efficient adsorption and charge transfer. This has been proposed to be a key mechanism in the catalytic activity of nonmetal heteroatom-doped graphene for oxygen reduction reaction.\textsuperscript{20} To account for this effect in TMC single layers, we have performed the Bader charge analysis evidencing that O heteroatoms form polar bonds with all investigated TMC hosts inducing a significant charge transfer. What is specific to our case is that O atoms embedded in various TMCs acquire electrons while becoming negatively charged. This is in contrast to conventional metal atom SACs that generally donate electrons to the substrate while becoming c$^-$ deficient. The anionic nature of heteroatom sites in 2D TMC crystals can be especially beneficial for catalyzing the hydrogen evolution reaction. Because screening in 2D crystals is significantly reduced, such sites with partially screened negative charges can provide an additional attractive interaction for the positively charged H species, facilitating their adsorption. According to the Bader charge analysis, the surplus of negative charge on the O atoms, which is defined by the extra charges compared to the pristine chalcogen atom charge, is expected to be the highest on tellurides and lowest on sulfides (Figure 2b), while it is practically unchanged for Mo and W compounds.

**Summary and Outlook.** 2D TMC materials emerge as an excellent active platform for single-atom catalysis, with the potential to overcome a series of scientific and technological challenges. The 100% atom utilization combined with a high coverage density opens the way toward the development of highly efficient catalysts. On the basis of our results, we propose that heteroatom doping is an efficient general approach to prepare single-site catalysts and activate the...
basal plane of a wide range of TMC single layers. This has been experimentally demonstrated previously for O-doped MoS$_2$ single layers. However, there is a lot of room for further investigation and optimization. One can vary the TMC substrate as well as the heteroatom dopant to increase the activity and optimize the selectivity for a given reaction. Investigating various 2D TMC crystals with O active sites can provide valuable information on the role of basal plane activation. Furthermore, in contrast to metal SACs that are of cationic nature, O dopants of various TMC single layers have an anionic character, enabling novel catalytic pathways. One can also use these oxygen-doped 2D TMC phases as a starting material and exchange oxygen dopants to other heteroatoms. With metal heteroatoms it is expected to reach higher SAC activity, but nonmetal dopants with markedly different electronegativity compared to host chalcogenide atoms are also expected to display a significant activity. Exploring nonisoelectronic heteroatom dopants can open new catalytic pathways with more complex mechanisms because of the electronic defect states emerging in the band gap. Besides the hydrogen evolution discussed here, by properly choosing the heteroatom, other reactions can also be catalyzed. For example, nitrogen or transition metal substitutions are expected to enhance the activity of MoS$_2$ monolayer-based catalysts for the oxygen reduction reaction based on recent computational studies.

A major advantage of combining single-atom catalysts with 2D crystal substrates is that the whole structure is fully accessible to atomic resolution local probe techniques, such as scanning tunneling microscopy. This allows atomic level insights in optimizing the catalyst structure. Such data are expected to be of key importance for understanding the structure–activity–selectivity relationships at the atomic level, answering key questions, such as the contribution of the heteroatoms and neighboring host atoms to the catalytic process. 2D solid solution TMCs with identical active sites of fully characterized atomic and electronic structure are expected to open a new chapter in the understanding and rational design of single-atom catalysts.
METHODS

Quantum-chemical modeling was performed within the framework of DFT using plane-wave basis set and the projector augmented wave method as implemented in VASP.\textsuperscript{45,46} The generalized gradient approximation (GGA) was used in the form of the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional.\textsuperscript{47} The plane wave basis cutoff energy $E_{\text{cutoff}}=450$ eV was used.\textsuperscript{46,47} To investigate defective structures, the $4 \times 4 \times 1$ supercells of MX$_2$ were used. In all geometry optimizations the convergence criterion was such that the maximal force acting on any atom was less than 0.01 eV/Å. The technical details of the Gibbs free energy calculations and Bader charge analysis can be found in ref 17 and references within.

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Notes
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