Magnetic MoS$_2$ pizzas and sandwiches with Mn$_n$ (n = 1–4) cluster toppings and fillings: A first-principles investigation

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The inorganic layered crystal (ILC) MoS$_2$ in low dimensions is considered as one of the most promising and efficient semiconductors. To enable the magnetism and keep intrinsic crystal structures, we carried out a first-principles study of the magnetic and semiconductive monolayer MoS$_2$ adsorbed with the Mn$_n$ (n = 1–4) clusters, and bilayer MoS$_2$ intercalated with the same clusters. Geometric optimizations of the Mn$_n$@MoS$_2$ systems show the complexes prefer to have Mn$_n$@MoS$_2$(M) pizza and Mn$_n$@MoS$_2$(B) sandwich forms in the mono- and bi-layered cases, respectively. Introductions of the clusters will enhance complex stabilities, while bonds and charge transfers are found between external Mn clusters and the S atoms in the hosts. The pizzas have medium magnetic moments of 3, 6, 9, 4μ$_B$ and sandwiches of 3, 2, 3, 2μ$_B$ following the manganese numbers. The pizzas and sandwiches are semiconductors, but with narrower bandgaps compared to their corresponding pristine hosts. Direct bandgaps were found in the Mn$_n$@MoS$_2$(M) (n = 1,4) pizzas, and excitingly in the Mn$_1$@MoS$_2$(B) sandwich. Combining functional clusters to the layered hosts, the present work shows a novel material manipulation strategy to boost semiconductive ILCs applications in magnetics.

Since a pioneering (re)discovery of the monolayer graphene$^{1,2}$, enormous researches have been focused on layered crystals during the past decades$^3$. Benefiting from covalence bonds in layers and van der Waals forces among layers, complex structures are easily manipulated in order to reach different application purposes. In contrast to the semimetallic pristine graphene, most of the inorganic layered crystals (ILCs) have non-zero bandgaps. Such semiconducting properties are essential in semiconductor industry. Various species from the nitrides and group VI metal compounds$^4$ enrich the library of the ILCs. Among them, the MoS$_2$ is a conventional lubricant$^5$ and catalyst for hydrogen evolution$^6,7$. When lowering the MoS$_2$ dimensions, a transition of indirect to direct band occurs, leading to the boosting of photoluminescence$^8,9$. Recent investigations of the materials in low dimensions showed that it is advanced in high efficient transistors$^{10}$, photoelectric devices$^{11}$, and electrocatalysis$^{12}$. To improve the performances of the MoS$_2$-based devices, molecular modulation and engineering are proposed and many of works are in progresses$^{13,14}$. Ideally speaking, the ILC materials can be piled up to 3D forms, with each 2D layer consisting of enough functional units such as doped atoms or clusters$^8$. So is the few-layer MoS$_2$, which has potentials in various applications and was reported as a key material in high mobility and low power transistors$^{15,16}$.

Pursuing semiconductors with high performances has always been within the focuses of materials sciences. Due to possible manipulations of electron spins and carrier intensities$^{17}$, dilute magnetic semiconductors (DMSs) have been one of the key targets within such an issue. Similar to the hosting merits from the transition metal (TM) oxides (say the ZnO)$^{17}$, the structural uniqueness of ILCs makes such layered groups as new candidate matrixes in the magnetic semiconductors. The 2D DMS systems have been explored in monolayer MoS$_2$, e.g., by substituting Mo ions with 3$d$ TMs$^{18,19}$ or 4$d$ TMs$^{20}$. The doping routes in the ILCs are, nevertheless, not an easy task in

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experiments. Alternatives were suggested to replace both Mo and neighboring S atoms with the FeX₆ (X = S, C, N, O, F) clusters, or a wetting deposition of the Co layer onto monolayer MoS₂. Brewing magnetism into double- or few-layered MoS₂ are rather scarcely reported, despite of the magnification of efficiencies in the 3D piled-up electronics. In a latest work, the Fe doped double layered MoS₂ was predicted to enhance the host stabilities as well as to magnetically exchange coupling between the host and dopants. However, doping or growing dynamics of such hetero functional units normally debuts from a fast nucleation of the metallic ions, resulting in rather small clusters or nanoparticles on the layered crystal surfaces or possibly among the layers. Indeed, in addition to clusters’ inimitable properties, combining clusters with the monolayer graphene was predicted to increase the magnetic moment of the cluster. Furthermore, the intercalated water molecules between graphene interlayers were observed experimentally and very unique properties have been revealed recently. Thus, in an analogy to routes of clusters anchoring on the graphene, using the clusters as dopants onto or among the ILCs may offer another effective route to tailor the ILCs properties.

In this article, we reported on a first-principles prediction of magnetic monolayer MoS₂ ‘pizzas’ with Mnₙ (n = 1–4) ‘toppings’, and bilayer MoS₂ ‘sandwiches’ with Mnₙ (n = 1–4) clusters ‘fillings’. The manganese clusters were selected as the start clusters due to their magnetic robustness, size-dependent magnetism, as well as easier adsorptions on layered structures. Hosts of the clusters were extended from monolayer MoS₂ ‘crust’ to the bilayer ‘bread slices’. To keep the intrinsic layered structures and prevent introducing defects, the clusters were placed and adsorbed on the top or between the layers. We investigated magnetic properties and electronic structures of the cluster adsorbed mono- and bi-layers. Bonding mechanisms within Mn clusters, and between clusters and ILC hosts were studied. In addition to possible variations of magnetic moments by changing the cluster sizes, we also found that introductions of the clusters into the ILC systems will facilitate system stabilities, and operate band types.

**Results**

**Geometric structures of the complexes.** Investigations of the doped system’s properties debut from the geometric structures. The free Mnₙ clusters were firstly studied to give basic knowledge of the ‘toppings’ or ‘fillings’ onto or into the crusts or bread slices. More than 60 initial Mnₙ structures were collected for further DFT optimization. Optimized clusters geometries were depicted in Fig. 1a. Detailed structural parameters for other low-lying isomers are provided in the Supplementary Information (SI). The Mnₙ clusters evolved from 0D to 2D forms when n was tuned from 1 to 3. However, in the case of n = 4, the 3D tetrahedron cluster was found as the most stable isomer, followed by a rhombus with a relative energy of 0.17 eV higher. Our results of free Mn clusters are in agreement with the previous DFT calculations.
Fig. 1c shows.

In this case of evenly numbered n, each Mn atom is bonded to four host S atoms and one Mo atom as complexes. In this case of inserting Mnn to bilayer MoS2 systems, the lowest energy structures exhibit odd-even alternations with the number of the Mn atoms. One Mn atom laying under the Mo atom (labelled 1 in Fig. 1c) is the lowest energy stable with higher energy as shown in Fig. 1b. On the contrary, the structure of the three-dimensional tetrahedron Mn4 cluster sandwiched between two layers of the MoS2 is unstable according to our calculation. In the figures, the dash-dot balls and lines refer to metastable positions of the Mnn clusters on the monolayer MoS2. However, in the ‘pizza’ and ‘sandwich’ cases. These participator S atoms interact with the impurity Mn n clusters, weakening bonding between the S and Mo atoms. On the contrary, the bond length of spectator atoms is the same as the one of the pristine MoS2. The Mn-Mn bond lengths in ‘pizzas’ and ‘sandwiches’, except for the Mn4@MoS2(M) and Mn4@MoS2(B) for the Bilayer ones. After a full optimization of all possible motifs including magnetic order effects, it is found that the Mn n@MoS2(M) prefer planar arrangements of the Mnn clusters with respect to the ILC hosts. In what follows, we name the systems of Mnn@MoS2(M) for the Mn n cluster doped Monolayer complexes, and Mnn@MoS2(B) for the Bilayer ones. From the hosts’ side, the 5 × 5 supercells of single- and two-layer MoS2 were firstly relaxed and the optimized results were shown on the left row in Fig. 1b,c. The lattice constants are 3.21 and 3.20 Å for the monolayer and bilayer MoS2, respectively, in good agreements with other density functional theory (DFT) calculations42. In general, the energy and magnetic properties of the Mn n@MoS2 systems are sensitive to coordination and contact positions of the Mnn clusters and their hosts were studied in details. For the Mnn@MoS2(M), the most stable adsorption sites of the Mn atoms are right above the Mo atom (numbered 1 in Fig. 1b) from the top view. Other possible adsorption sites on-top S atom, bridge and face as labelled 2, 3, and 4 in Fig. 1b are energetically unfavorable. Our optimizations show that each Mn adatom is bonded to three S atoms at the monolayer MoS2 site. For the Mnn@MoS2(M), the most stable structure is constructed by the tetrahedron Mnn cluster whose triangular face lays on the MoS2 host. The rhombic structure with four Mn atoms tiled above the Mo site is less stable with higher energy as shown in Fig. 1b. On the contrary, the structure of the three-dimensional tetrahedron Mnn cluster sandwiched between two layers of the MoS2 is unstable according to our calculation. In the figures, the dash-dot balls and lines refer to metastable positions of the Mnn clusters on the monolayer MoS2. However, in the case of inserting Mn n to bilayer MoS2 systems, the lowest energy structures exhibit odd–even alternations with the number of the Mn atoms. One Mn atom laying under the Mo atom (labelled 1 in Fig. 1c) is the lowest energy structures of odd number n with each adatom Mn bonding six S atoms in the bilayer MoS2, while the Mn atoms preferring to be under the S atom (featured 2 in Fig. 1c) and forming the most stable Mn n@MoS2(B) (n = 1–4) complexes. In this case of evenly numbered n, each Mn atom is bonded to four host S atoms and one Mo atom as Fig. 1c shows.

### Bonding scheme and stability

Table 1 gives bond lengths of the Mn n clusters adsorbed on the monolayer and bilayer MoS2 at the most stable adsorption sites. Two kinds of hosting atoms are classified: participators with whom dopants are bonded, and spectators where no additional bonding are formed. The MoS2 honey comb structures remain unchanged after absorptions of the Mn n clusters. Very slight lattice distortions are found at the participant area near the Mn n clusters. From Table 1, it can be seen that the distances of the d Mn–Mo, between the participator atoms of the MoS2 became larger than those of the pristine MoS2 in both the ‘pizza’ and ‘sandwich’ cases. These participator S atoms interact with the impurity Mn n clusters, weakening bonding between the S and Mo atoms. On the contrary, the bond length of spectator atoms is the same as the one of the pristine MoS2. The Mn–Mn bond lengths in ‘pizzas’ and ‘sandwiches’, except for the Mn4@MoS2(M) and Mn@MoS2(M), are notably larger than those in the free Mn n clusters, also indicating a covalent-bond interaction between the Mn and S atoms. The Mn–Mo bond lengths in Mn2@MoS2(B) and Mn@MoS2(B) are 2.762 and 2.897 Å, respectively. Notably, values of the farthest d Mn–S in Mn2@MoS2(B) oscillate with the Mn numbers. The oscillating trend pervades to electronic and magnetic properties of the Mn n@MoS2 (B) sandwiches in the follow discussion.

The adsorption energies E ad of the Mn n clusters adsorbed on the ILC hosts were computed as follows.

\[
E_{\text{ad}} = E_{\text{total}}(\text{Mn}_n@\text{MoS}_2) - (E_{\text{total}}(\text{MoS}_2) + E_{\text{total}}(\text{Mn}_n)),
\]

| Layer Number | System Name | Optimized bond distance (Å) | E ad (in eV) |
|--------------|-------------|----------------------------|-------------|
|              |             | d Mn–Mo (nearest) | d Mn–S (farthest) | E ad (in eV) |
| 0            | Mn cluster  | — | 2.437 | — |
| 1            | Mn4@MoS2    | 2.897 | 2.556 | —4.207 |
|              | Mn3@MoS2    | 2.631 | 2.531 | —4.725 |
|              | Mn2@MoS2    | 2.791 | 2.457 | —6.297 |
|              | pristine    | — | 2.432 | — |
| 2            | Mn4@MoS2    | 2.917 | 2.578 | —5.013 |
|              | Mn3@MoS2    | 2.956 | 2.457 | —6.227 |
|              | Mn2@MoS2    | 2.940 | 2.469 | —8.787 |

Table 1. Adsorption energies E ad (in eV) and bond lengths d (in Å) of the Mn n (n = 1–4) clusters adsorbed on the monolayer and bilayer MoS2. The MoS2 layer number was set 0 for the free manganese clusters.
moment of 6.3

DED distributes not only surrounding the Mo and S atoms in the host MoS2 but also remarkably at the
isolated Mn7 cluster. In the case of Mn doped MoS2 studied through a combination of DFT calculations and
MoS2. The Mnn@MoS2(M) pizzas prefer to have medium magnetic moments of 3, 6, 9, and 4
energetic magnetic spin state displays ferrimagnetic properties when ferromagnetic Mn clusters adsorbed on the
spin states of the Mnn clusters adsorbed on the ILC hosts at the lowest energy adsorption sites. Results show that
of the magnetic guests. For this purpose, we optimized all magnetic spin states of the lowest-energy structures
were investigated by first-principles calculations. The total magnetic moments of H-, B-, C-, N-, and F-adsorbed
MoS2 monolayers were found 1, 1, 2, 1, and 1 μB, respectively. The magnetic motifs of all
these three cases are different from that of the Mnn@MoS2 ‘pizzas’ and ‘sandwiches’ studied here. By comparing
the magnetic properties between other cases and this work, more insights may be provided into the effect of the
impurities types employed on a nonmagnetic layer host.

Magnetic properties. The lowest-spin arrangements of individual clusters are all ferromagnetic from our
present calculations. Magnetic moments of the Mnn (n = 1–4) clusters are 5, 10, 15, and 20 μB, respectively, in
agreement with previous studies. It is important to understand the host influence on the magnetic orders of
the magnetic guests. For this purpose, we optimized all magnetic spin states of the lowest-energy structures of
the ‘pizzas’ and ‘sandwiches’ from Fig. 1b,c. Table 2 gives the relative energies with respect to the most stable
spin states of the Mnn clusters adsorbed on the ILC hosts at the lowest energy adsorption sites. Results show that
magnetic moments of the impurity Mnn clusters are not quenched by the nonmagnetic host MoS2 substrate. The
energetic magnetic spin state displays ferrimagnetic properties when ferromagnetic Mn clusters adsorbed on the
MoS2. The Mnn@MoS2(M) pizzas prefer to have medium magnetic moments of 3, 6, 9, and 4 μB in comparison
with their corresponding free Mnn clusters (5, 10, 15, 20 μB). The Mnn@MoS2(B) sandwiches exhibit favorable
oscillatory behavior with relatively smaller magnetic moments of 3, 2, 3, and 2 μB. To reveal detailed contributions
from each Mn atom in the ‘topping’ or ‘fillings’, we also studied the local spin state on the Mn atom of the
Mnn@MoS2 (M&B) systems. Their magnetic moments are listed in Table S1 (see details in SI). The Mn atoms in
Mnn@MoS2(M) pizzas are in ferromagnetic states except for theses of the Mnn@MoS2(M). On the Mnn@MoS2(M)
pizza, three tiled Mn atoms have “spin-up” (majority) magnetic moments and one top Mn atom has “spin-down”
(minority) magnetic moments. While in the Mnn@MoS2(B) sandwiches, the Mn atoms display ferrimagnetic
order as shown in Table S1. Thus the guest Mnn clusters may serve as an ideal system to tailor magnetic properties
when introduced on or between the MoS2 ‘crust’ or ‘bread slices’. Continued experimental and theoretical studies of
similar TM clusters adsorbed on MoS2, systems may lead to discoveries of new families of dilute magnetic sem-
conductors with tunable magnetic properties.

It should be noted that the magnetic properties of the Mn7 cluster absorbed on graphene exhibits a magnetic
moment of 6.3 μB per cell as given by first-principles calculations. This value is 1.3 μB larger than 5.0 μB in an
isolated Mn7 cluster. In the case of Mn doped MoS2 studied through a combination of DFT calculations and
Monte Carlo simulations, the overall magnetic moment of the supercell is 1 μB corresponding to the single excess
d electron provided by the Mn atom. On the other hand, magnetic properties of nonmetal atoms adsorbed
MoS2 monolayers were also investigated by first-principles calculations. The total magnetic moments of H-, B-,
C-, N-, and F-adsorbed MoS2 monolayers were found 1, 1, 2, 1, and 1 μB, respectively. The magnetic motifs of all
these three cases are different from that of the Mnn@MoS2 ‘pizzas’ and ‘sandwiches’ studied here. By comparing
the magnetic properties between other cases and this work, more insights may be provided into the effect of the
impurities types employed on a nonmagnetic layer host.

Mulliken population analysis shows that the total magnetic moment of the clusters is mainly localized in the
Mn atoms as tabulated in Table 3. A small amount of magnetic moment is found in host Mo and S atoms. To

Figure 2. Electron densities of the Mnn@MoS2(M) complex. (a) The deformation electron density (DED).
Charge accumulations are obvious in blue regions and depletions in silvery regions. (b) Total electron density.
(c) The net spin electron density. The surface isovalue for electron density is 0.04 e/Å3.
visualize the spin distribution of the Mn_n@MoS_2(M) ‘pizza’, the isosurface spin density of the ‘pizza’ was plotted in Fig. 2. It can be seen from Fig. 2b,c that although the total charge density is extended over the whole Mn_3@MoS_2(M), the spin density is almost entirely located on the Mn_3 cluster site, resulting in a robust magnetic moment of 9 \( \mu_B \) for the Mn_3@MoS_2(M).

**Electronic structures.** The band structures of the Mn_n@MoS_2(M&B) complexes were plotted in Fig. 3 for the lowest-energy structures. These from the pristine monolayer and bilayer MoS_2 were also given for comparison.

### Table 2. Magnetic moments \( M (\mu_B) \) of the Mn_n cluster adsorbed MoS_2 complexes. Metastable isomers of other magnetic moments have different relative energies of \( \Delta E \) (in eV) with respect to the most stable ones. The hyphen (—) means the structure is not converged during the optimization.

| System       | Mn@MoS_2(M) | Mn@MoS_2(B) | Mn_2@MoS_2(M) | Mn_2@MoS_2(B) | Mn_3@MoS_2(M) | Mn_3@MoS_2(B) | Mn_4@MoS_2(M) | Mn_4@MoS_2(B) |
|--------------|-------------|-------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Monolayer    |             |             |               |               |               |               |               |               |
| \( M (\mu_B) \) | \( \Delta E \) (eV) | \( M (\mu_B) \) | \( \Delta E \) (eV) | \( M (\mu_B) \) | \( \Delta E \) (eV) | \( M (\mu_B) \) | \( \Delta E \) (eV) | \( M (\mu_B) \) | \( \Delta E \) (eV) |
| 1            | 0.62        | 1           | 0.25          | 1             | 0.09          | 2             | 0.15          | 10            | 1.29          |
| 3            | 0           | 3           | 0             | 3             | 0             | 3             | 0             | 8             | 0.63          |
| 5            | 0.23        | 5           | 0.15          | 5             | 0.07          | 6             | 0.15          | 10            | 1.29          |
| Bilayer      |             |             |               |               |               |               |               |               |               |
| \( M (\mu_B) \) | \( \Delta E \) (eV) | \( M (\mu_B) \) | \( \Delta E \) (eV) | \( M (\mu_B) \) | \( \Delta E \) (eV) | \( M (\mu_B) \) | \( \Delta E \) (eV) | \( M (\mu_B) \) | \( \Delta E \) (eV) |
| 0            | —           | 0           | 0             | 0             | 0             | 0             | 0             | 0             | 0             |
| 2            | 0.09        | 2           | 0             | 2             | 0             | 2             | 0             | 10            | 1.29          |
| 4            | 0.31        | 4           | 0.15          | 4             | 0.07          | 6             | 0.15          | 10            | 1.29          |
| 6            | 0           | 6           | 0             | 6             | 0.09          | 8             | 0.63          | 10            | 1.29          |
| 8            | 0.07        | 8           | 0.63          | 8             | 0.07          | 10            | 1.29          | 10            | 1.29          |
| 10           | 0.32        | 10          | 1.29          | 10            | 0.32          | 10            | 1.29          | 10            | 1.29          |

### Table 3. Charge transfer and local magnetic moments of the Mn_n cluster adsorbed MoS_2 complexes. Mulliken Charge (in au) were counted on the Mn atoms, local magnetic moment (in \( \mu_B \)) on the guest Mn clusters, host Mo and S atoms. Total magnetic moment (in \( \mu_B \)) and bandgap (in eV) of the Mn_n clusters absorbed on monolayer and bilayer MoS_2 per supercell were also tabulated herein.

| System       | Mn@MoS_2(M) | Mn@MoS_2(B) | Mn_2@MoS_2(M) | Mn_2@MoS_2(B) | Mn_3@MoS_2(M) | Mn_3@MoS_2(B) | Mn_4@MoS_2(M) | Mn_4@MoS_2(B) |
|--------------|-------------|-------------|---------------|---------------|---------------|---------------|---------------|---------------|
| pristine     | —           | 0           | 0             | 0             | 0             | 0             | 1.687         |
| Mn@MoS_2(M)  | 3.26        | -0.132      | -0.128        | 3             | 0.053         | 0.463         |
| Mn_2@MoS_2(M)| 6.706       | -0.502      | -0.204        | 6             | -0.07         | 0.327         |
| Mn_3@MoS_2(M)| 9.578       | -0.362      | -0.216        | 9             | -0.175        | 0.245         |
| Mn_4@MoS_2(M)| 4.579       | -0.51       | -0.069        | 4             | -0.215        | 0.137         |
| pristine     | —           | 0           | 0             | 0             | —             | 1.144         |
| Mn@MoS_2(B)  | 2.881       | 0.027       | 0.092         | 3             | -0.32         | 0.272         |
| Mn_2@MoS_2(B)| 2.042       | -0.016      | -0.026        | 2             | -0.771        | 0.490         |
| Mn_3@MoS_2(B)| 3.195       | -0.224      | 0.029         | 3             | -0.808        | 0.245         |
| Mn_4@MoS_2(B)| 1.953       | 0.147       | -0.1          | 2             | -1.715        | 0.276         |
purposes. In the monolayer, a direct bandgap was found to have energies of 1.69 eV and 1.89 eV in our GGA and Heyd-Scuseria-Ernzerhof (HSE06) calculations implemented in CASTEP package. The values are in good agreement with previous studies. Although GGA at the PBE level calculations typically underestimates this bandgap, there is no difference between the GGA and HSE06 evaluations of the bandgap types. As Fig. 3 shows, the embedment of the Mn clusters inserts additional defect states within the pristine MoS₂ bandgap. The valence band maximum (VBM) and conduction band minimum (CBM) are primarily from the 3d orbitals of the Mn clusters. The partial density of states (PDOS) of Mn@MoS₂ in Fig. 4 clarifies those defect states are from the Mn clusters near the VBM and the CBM. Compared with the pristine MoS₂ cases, Fermi energy shifts from the VBM towards the CBM with the increase of the Mn numbers. Figure 4 also shows that shapes of the total density of states for α electron (spin-up) and β electron (spin-down) near the Fermi energy are quite different in the contributions of the magnetism of the Mn@MoS₂. The bandgap of the pristine MoS₂ is evidently reduced due to the absorptions of small TM clusters. Such a reduction can significantly affect material optical and transport properties. From the values listed in Table 3, the bandgap of the ‘pizzas’ decreases gradually with the successive Mn atoms. However, odd-even oscillation emerges again in bilayer system similar to its magnetic properties.

As the Mn clusters are adsorbed on MoS₂, there is obvious hybridization between the atomic orbitals of the guest atom Mn and host atom S. We take the PDOS plots of Mo, S, and Mn atoms of the Mn@MoS₂(M) as an example (see Fig. 5) to explicate the hybridization. Several sharp peak superpositions originate from the PDOS for d orbital of Mn and p orbital of S in the S-Mn bond below the Fermi level. And the PDOS for Mo and S atoms in S-Mo bond close to the Mn cluster is quite different from these spectator Mo and S atoms far away the Mn cluster. Similar behavior is observed in all other Mn@MoS₂ systems.

Figure 3. Spin-polarized band structures of the Mnₙ adsorbed MoS₂ systems. (a) Band structures of the Mnₙ@MoS₂ pizzas. (b) Band structures of the Mnₙ@MoS₂ sandwiches. The blue and magenta lines represent the spin-up and spin-down components, respectively. The horizontal dash-dot lines indicate the Fermi level. The band structures of the pristine hosts are depicted at the very left column for comparison purpose.
Figure 4. Electronic partial density of states (PDOS) of the Mn adsorbed MoS$_2$ systems. (a) The PDOS of spin-up (positive) and spin-down (negative) electrons of the Mn$_n$@MoS$_2$ (M) pizzas. (b) The PDOS of spin-up (positive) and spin-down (negative) electrons of the Mn$_n$@MoS$_2$ (B) sandwiches. The PDOS is obtained by Gaussian extension applied to the eigenvalues with a broadening width of 0.1 eV. The vertical dash-dot lines indicate the Fermi level.
Types of bands can be switched through the present doping route. A transition from an indirect to a direct bandgap in pristine MoS$_2$ are found when the thickness is reduced from bilayer to a monolayer, in agreement with previous experimental reports$^{9,56}$ and theoretical results$^{57,58}$. After the Mnn clusters were introduced to the host MoS$_2$ 'crusts', the Mnn@MoS$_2$(M) pizza (n = 1,4) bandgaps keep direct as their host's. However, the bandgap turns to indirect when n = 2,3 as shown in Fig. 3a. Excitingly, in the case of the Mn$_1$@MoS$_2$(B) 'sandwich', the indirect bandgap of the bilayer host was switched to a direct bandgap. The CBM and VBM are both aligned at the $\kappa$ point. Such a direct band structure is similar to the monolayer's ones, which have been considered as the crucial origin of the ILC unique material properties. The result indicates the bandgap of pristine MoS$_2$ can be operated from an indirect to direct or direct to indirect bandgap by adsorbing small TM clusters like Mn$_n$. This provides new opportunities for controlling electronic structures in nanoscale materials with novel optical behaviors.

Ranging from 0.053 to −0.215 and −0.32 to −1.715 au in the 'pizza' and 'sandwiches' systems, the net charge on the impurity Mn clusters clearly shows charge transfers between the 'toppings' and 'fillings', and the S atoms in the 'crusts' and 'slices'. This leads high stabilities of the 'pizza' and 'sandwiches' following the partially ionic-like bonding of the Mn−S interaction through the charge transfers. Except for the Mn$_1$@MoS$_2$(M), charge transfers occur from the S atoms to the Mn atoms resulting in negative charges of the Mnn clusters. For the Mnn@MoS$_2$(B), increases of the net charge values on the Mn clusters were found, illustrating enhancements of the sandwiches structures as the successive add-on dopant. The charge transfers between the Mn clusters and host MoS$_2$ are one reason of the reducing magnetic moment of Mn$_n$@MoS$_2$ from the isolate Mn clusters, while strong hybridizations of the sulfur atoms in the MoS$_2$ with the d states of the Mn cluster atoms is counted as another.

Thermostabilities. The thermodynamic stability was tested by using the Born–Oppenheimer molecular dynamics simulation implemented in the DMOL3 code at room temperature (T = 300 K). A sample of the dynamic simulations is shown in Fig. 6 for the Mn$_1$@MoS$_2$(M) pizza case. It is clear that the relative potential energy remains unchanged within the selected time scale. The ground-state structure is stable at room temperature. Such a thermostability is in line with the experimental evidences of the Au adsorbed MoS$_2$ monolayer$^{59}$ and the latest results of the water intercalated organic counterpart of the graphene$^{55}$.
Figure 6. Relative potential energy (eV) of the lowest-energy structures Mn₄@MoS₃(M). The simulation time was set to 3 ps at a step interval of 1 fs in the molecular dynamics simulation.

In conclusion, we have presented a new strategy of tailoring the inorganic layered crystal to the magnetic semiconductors by introducing magnetic clusters as adsorbates. Geometric optimizations show that the small clusters prefer to follow the host alignments to enhance the complex stabilities. The magnetic and electronic structures were thoroughly explored. It is found that the system magnetic properties and electronic structures can be manipulated by careful selections of the ‘pizza’ and ‘sandwich’ recipes. Moreover, switches between the direct and indirect bandgaps of the adsorbed MoS₂ complexes were revealed. Benefiting from the uniqueness of the clusters and inorganic layered crystals, it is hoped that the present work will be served as a prototype in combinations of the cluster and layered crystal sciences, and boost their applications in the semiconducting scopes.

Methods
All calculations were performed by using the DMOL3 package⁶⁰. Results from the present package were cross checked with the calculations from CASTEP package. A relativistic semi-core pseudopotential was employed for the spin-unrestricted calculations with double-numerical basis where d polarization functions (DNP) were included. Generalized gradient approximation in the Perdue – Ernzerhof (PBE) functional form was chosen.⁶² The effect of van der Waals interactions was introduced explicitly through an empirical correction scheme proposed by Ortmann, Bechstedt, and Schmid.⁶³ The quality of the self-consistent field (SCF) convergence tolerance was set as “fine”. A convergence criterion of 1 × 10⁻³ hartree/Å on the gradient, and 5 × 10⁻⁴ Å on lattice displacements. The 5 × 5 supercells were constructed from 75 atoms of 25 Mo atoms and 50 S atoms for the monolayer, and 150 atoms including 50 Mo atoms and 100 S atoms for the bilayer. A vacuum region of 25 Å was selected in the z-direction to exclude mirror interactions between neighboring images. The Brillouin Zone integrations were carried out on a 10 × 10 × 1 Monkhorst-Pack k-points grid for the geometry optimizations, and a 15 × 15 × 1 k-points grid for the band and density of states (DOS) properties. To elucidate system magnetic properties, we carried out a detailed calculation for each possible spin multiplicity (SM) ranging from 1 to 21 of the Mₙₙ (n = 1–4) adsorbed MoS₂ complexes.

References
1. Novoselov, K. S. et al. Electric field effect in atomically thin carbon films. Science 306, 666–669 (2004).
2. Novoselov, K. S. et al. Two-dimensional gas of massless Dirac fermions in graphite. Nature 438, 197–200 (2005).
3. Geim, A. K. Grahe of status and prospects. Science 324, 1530–1534 (2009).
4. Geim, A. K. & Grigorieva I. Van der Waals heterostructures. Nature 499, 419–425 (2013).
5. Cohen, S. R. et al. The tribological behavior of type II textured MX₂ (M = Mo, W, X = S, Se) films. Thin Solid Films 324, 190–197 (1998).
6. Furimsky, E. Role of MoS₂ and WS₂ in hydrosulfurization. Catal. Rev. 22, 371–400 (1980).
7. Hinnemann, B. et al. Biomimetic hydrogen evolution: MoS₂ nanoparticles as catalyst for hydrogen evolution, J. Am. Chem. Soc. 127, 5308–5309 (2005).
8. Splendiani, A. et al. Emerging photoluminescence in monolayer MoS₂, Nano Lett. 10, 1271–1275 (2010).
9. Mak, K. F. Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically thin MoS₂: A new direct-gap semiconductor. Phys. Rev. Lett. 105, 136805 (2010).
10. Kim, S. et al. High-mobility and low-power thin-film transistors based on multilayer MoS₂ crystals. Nat. Commun. 3, 1011 (2012).
11. Lopez-Sanchez, O., Lembke, D., Kayci, M., Radenovic, A. & Kis, A. Ultrasensitive photodetectors based on monolayer MoS₂, Nat. Nanotechnol. 8, 497–501 (2013).
12. Kübgaard, J., Chen, Z., Reinecke, B. N. & Jaramillo, T. F. Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis. Nat. Mater. 11, 863–869 (2012).
13. Butler, S. Z. et al. Progress, challenges, and opportunities in two-dimensional materials beyond graphene. ACS Nano 7, 2898–2926 (2013).
14. Lee, Y. H. et al. Synthesis of large-area MoS₂ atomic layers with chemical vapor deposition. Adv. Mater. 24, 2320–2325 (2012).
15. Ganatra, R. & Zhang, Q. Few-layer MoS₂: A promising layered semiconductor. ACS Nano 5, 4074–4099 (2011).
16. Dietl, T., Ohno, H., Matsukura, F., Cibert, J. & Ferrand, D. Zener model description of ferromagnetism in zinc-blend magnetic semiconductors. Science 287, 1019–1022 (2000).
17. Chambers, S. A. Ferromagnetism in doped thin-film oxide and nitride semiconductors and dielectrics. Surf. Sci. Rep. 61, 345–381 (2006).
25. Park, J., Privman, V. & Matijević, E. Model of formation of monodispersed colloid. (2014).

26. Liu, A. H., Salabas, E. L. & Schuth, F. Magnetic nanoparticles: synthesis, protection, functionalization, and application. Angew. Chem. Int. Ed. 46, 1222–1244 (2007).

27. Cheng, F., Chen, J. & Gou, X. MoS2-Ni nanocomposites as catalysts for hdrodesulfurization of thiophene and thiophene derivatives. Adv. Mater. 18, 2561–2564 (2006).

28. Sarkar, D. et al. Functionalization of transition metal dichalcogenides with metallic nanoparticles: Implications for doping and gas-sensing. Nano Lett. 15, 2852–2862 (2015).

29. Cao, W. et al. Gold nanoparticles on MoS2 layer: Crystalline phase. Mater. Chem. Phys. 158, 89–95 (2015).

30. Krotos, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F. & Smalley, R. E. C60: Buckminsterfullerene. Nature 318, 162–163 (1985).

31. Pykkylö, P. Structural properties: Magic nanoclusters of gold. Nat. Nanotechnol. 2, 273–274 (2007).

32. Liu, X., Wang, C. Z., Lin, H. Q. & Ho, K. M. Magnetic moment enhancement for Mn7 cluster on graphene. New J. Phys. 15, 033025 (2015).

33. Wang, G. et al. Nickel cluster growth of sites for graphene: A computational study. Angew. Chem. Int. Ed. 52, 14237–14241 (2013).

34. Algara-Siller, G. et al. Square ice in graphene nanocapillaries. Nature 519, 443–445 (2015).

35. Zhang, M. et al. First-principles investigations of chirality in trimeric alloy clusters: AlMnAu n (n = 1–7). J. Phys. Chem. A 119, 3458–3470 (2015).

36. Bobadova-Parvanova, P., Jackson, K. A., Srinivas, S. & Horoi, M. Emergence of antiferromagnetic ordering in Mn clusters. Phys. Rev. A 67, 061202 (2003).

37. Rigo, V. A., Miwa, R. H., da Silva, A. J. R. & Fazzio, A. Mn dimers on graphene nanoribbons: An ab initio study. J. Appl. Phys. 109, 053715 (2011).

38. Kabir, M., Mookerjee, A. & Kanhere, D. G. Structure, electronic properties, and magnetic transition in manganese clusters. Phys. Rev. B 73, 224439 (2006).

39. Longo, R. C., Noya, E. G. & Gallego, L. I. Fully unconstrained density-functional study of the structures and magnetic moments of small Mn5 clusters (n = 2–7). Phys. Rev. B 72, 174409 (2005).

40. Gutsev, G. L., Mochena, M. D. & Bauschlicher, Jr. C. W. Structure and properties of Mnn, Mnn, S = 0, 1, and Mnn clusters (n = 3–10). J. Phys. Chem. A 110, 9758–9766 (2006).

41. Ataca, C. & Ciraci, S. Functionalization of single-layer MoS2 honeycomb structures. J. Phys. Chem. C 115, 13303–13311 (2011).

42. Ramasubramaniam, A. & Naveh, D. Mn-doped monolayer MoS2: An atomically thin dilute magnetic semiconductor. Phys. Rev. B 87, 195201 (2013).

43. He, I., Wu, K., Sa, R., Li, Q. & Wei, Y. Magnetic properties of nonmetal atoms adsorbed MoS2 monolayers. Appl. Phys. Lett. 96, 082504 (2010).

44. Bu, H. et al. Isoelectronic doping of graphdiyne with boron and nitrogen: Stable configurations and band gap modification. J. Phys. Chem. A 116, 3934 (2012).

45. Zhao, M., Dong, W. & Wang, A. Two-dimensional carbon topological insulators superior to graphene. Sci. Rep. 3, 3532 (2013).

46. Huang, H., Duan, W. & Liu, Z. The existence/absence of Dirac cones in graphdiyne. New J. Phys. 15, 023004 (2013).

47. Zhou, Y. G., Su, Q. L., Wang, Z. G., Deng, H. Q. & Zu, X. T. Controlling magnetism of MoS2 sheets by embedding transition-metal atoms and applying strain. Phys. Chem. Chem. Phys. 15, 18464–18470 (2013).

48. Terrones, H., López-Urias, F. & Terrones, M. Novel hetero-layered materials with tunable direct band gaps by sandwiching different metal disulides and diselenides. Phys. Rep. 535, 1–149 (2013).

49. Johari, P. & Shenoy, V. B. Tuning the electronic properties of semiconductor transition metal dichalcogenides by applying mechanical strains. ACS Nano 6, 5449–5456 (2012).

50. Yun, W. S., Han, S. W., Hong, S. C., Kim, I. G. & Lee, J. D. Thickness and strain effects on electronic structures of transition metal dichalcogenides: 2H-MX2 semiconductors (M = Mo, W; X = S, Se, Te). Phys. Rev. B 83, 033302 (2011).

51. Scalise, E., Houssa, M., Pourtois, G., Afanas’ev, V. & Stesmans, A. Strain-induced semiconductor to metal transition in the two-dimensional honeycomb structure of MoS2. Nano Res. 5, 43–48 (2012).

52. Han, S. W. et al. Band-gap transition induced by interlayer van der Waals interaction in MoS2. Phys. Rev. B 84, 045409 (2011).

53. Kuc, A., Zibouchou, N. & Heine, T. Influence of quantum confinement on the electronic structure of the transition metal sulfide TS2, Phys. Rev. B 83, 245213 (2011).

54. Ramasubramaniam, A., Naveh, D. & Towe, E. Tunable band gaps in bilayer transition-metal dichalcogenides. Phys. Rev. B 84, 205325 (2011).

55. Splendiani, A. et al. Emerging photoluminescence in monolayer MoS2, Nano Lett. 10, 1271–1275 (2010).

56. Ellis, J. K., Lucero, M. J. & Scuseria, G. E. The indirect to direct band gap transition in multilayered MoS2, as predicted by screened hybrid density functional theory. Appl. Phys. Lett. 99, 261908 (2011).

57. Cherwanchanamong, T. & Lambrecht, W. R. L. Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS2. Phys. Rev. B 85, 205302 (2012).

58. Lin, Y. C. et al. Properties of individual dopant atoms in single-layer MoS2: Atomic structure, migration, and enhanced reactivity. Adv. Mater. 26, 2857–2861 (2014).

59. Delley, B. An all-electron numerical method for solving the local density functional for polyatomic molecules. J. Chem. Phys. 92, 508–517 (1990).

60. Delley, B. From molecules to solids with the Dmol3 approach. J. Chem. Phys. 113, 7756–7764 (2000).

61. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).

62. Ortman, F., Bechstedt, F. & Schmidt, W. G. Semiempirical van der Waals correction to the density functional description of solids and molecular structures. Phys. Rev. B 73, 205101 (2006).
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The project was initiated by W.C. and conceived by W.C. and M.Z. M.Z. conducted the calculations. Z.H., X.W., H.Z., T.L., Z.W. and Y.L. participated in the calculations and structural optimizations. The article was written by M.Z. and W.C. All authors have read and commented on the manuscripts.

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