First-principles study of nonmetal doped monolayer MoSe$_2$ for tunable electronic and photocatalytic properties

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Recently, two dimensional transition metal dichalcogenides become popular research topics because of their unique crystal and electronic structure. In this work, the geometrical structure, electronic, electrical transport, redox potentials and photocatalytic properties of nonmetal (H, B, C, Si, N, P, As, O, S, Te, F, Cl, Br and I) doped monolayer MoSe$_2$ were investigated by first principle calculations. The binding energy indicates that nonmetal doped MoSe$_2$ are energetically favorable compared to Se vacancies, except B- and C-doped. We have found that nonmetal dopants with an even number of valence electrons doped MoSe$_2$ have p-type conductivity. On the contrary, nonmetal dopants with an odd number of valence electrons doped MoSe$_2$ have n-type or p-type conductivity; and they have better photocatalytic performance.

Transition metal dichalcogenides (TMDCs) have unique structural and electronic properties. Consequently, they possess various conducting properties that include insulating, semiconducting, conducting and even superconducting. And these cause potential applications in electronics, spintronics and optoelectronics$^{1-8}$. TMDCs family has more than 40 compounds (including MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$ and WTe$_2$, etc) with the formula of MX$_2$$^{9,10}$. These TMDCs materials have been obtained by micromechanical exfoliation or liquid exfoliation (due to the weak van der Waals bonding interactions in the adjacent sandwiched layers)$^{11-13}$, chemical vapor deposition (CVD)$^{14}$ and molecular beam epitaxy (MBE)$^{15,16}$. However, vacancies inevitably occur in the growth process of TMDCs$^{17-19}$.

The introduction of dopant atoms into the vacancies is considered as a promising method of modulating their electronic, magnetic and transport properties of monolayer TMDCs$^{20-29}$. Experimentally, Zn- and Co-doped MoS$_2$ nanosheets have been realized and demonstrate potential applications in the field of electronics, optoelectronics, spintronics and photocatalysis$^{30-31}$. Moreover, a series of work have reported that ultrathin N- and P-doped MoS$_2$ nanosheets have demonstrated enhanced hydrogen evolution reaction (HER) catalysis, enhanced oxygen reduction reaction (ORR) and efficient degradation of methyl orange and RhB, respectively$^{32-36}$. This is due to they can promote the charge transfer in the photocatalytic reaction. These results suggest that doping nonmetal (NM) atoms is an effective way to promote the catalytic performance.

However, the above articles lack the calculations on the electrical transport of NM doped systems. Moreover, systematically understanding the modification on the physical and chemical properties of the NM doped monolayer MoSe$_2$ is necessary. In this work, we provide a comprehensive investigation on the geometrical structure, binding energy, electronic, optical and photocatalytic properties of substitutionally doped monolayer MoSe$_2$ with a series of NM atoms, such as H, B, C, Si, N, P, As, O, S, Te, F, Cl, Br and I, by employing first-principle calculations. And we found the parity of the valence electrons of the dopants causes a dramatic difference on electrical transport, molecular state, redox potentials and photocatalytic activity.

Computational Methods

The geometrical structure, electronic and optical properties of undoped and NM doped monolayer MoSe$_2$ are calculated within the framework of density functional theory by using the CASTEP package. Norm-conserving
pseudopotentials and Perdew-Burke-Ernzerhof (PBE) function of the generalized gradient approximation (GGA) are used for the electron-ion interactions and exchange-correlation potential, respectively. The adopted monolayer structure is a $4 \times 4 \times 1$ supercell containing 16 Mo (blue ball), 31 Se (yellow ball) and 1 NM atoms (purple ball) (Fig. 1(a)). The high cutoff energy for the plane-wave basis is set at 750 eV and the Brillouin zone is sampled by a $9 \times 9 \times 1$ $k$-point sampling grid. A vacuum layer of 15 Å is adopted in the direction perpendicular to the monolayer surface to avoid the interactions between periodic slabs. The structural optimization is continued until the convergence tolerance of energy, maximum force and maximum displacement are less than $5.0 \times 10^{-6}$ eV/atom, 0.01 eV/Å and $1.0 \times 10^{-3}$ Å, respectively.

We have calculated the binding energies ($E_b$) of all the doped systems to assess the stability of doped MoSe$_2$:

$$E_b = E_{\text{vacany}} + \mu_{\text{NM}} - E_{\text{doped}}$$  (1)

Table 1. The equilibrium supercell lattice parameters $a$ with unit Å, $d_{\text{Mo-NM}}$ is the bond lengths of Mo-NM bonds with unit Å, $h$ is the sheet thicknesses from NM atom to the reference Mo atom plane with unit Å. $E_b$, $E_g$, $E_{\text{CBM}}$, and $E_{\text{VBM}}$ are the calculated binding energies, band gap, Fermi level, the energy edge of CBM and VBM relative to vacuum level, respectively, with unit eV.

| Dopant | $a$ (Å) | $d_{\text{Mo-NM}}$ (Å) | $h$ (Å) | $E_b$ (eV) | $E_g$ (eV) | $E_{\text{VBM}}$ (eV) | $E_{\text{CBM}}$ (eV) | $E_{\text{F}}$ (eV) |
|--------|--------|------------------------|--------|------------|------------|----------------|----------------|-------------|
| H      | 3.332  | 2.054                  | 0.888  | -3.00      | -3.95      | -2.29         | 1.66           |             |
| B      | 3.350  | 2.145                  | 0.801  | -3.75      | -4.00      | -2.35         | 1.65           |             |
| C      | 3.344  | 2.041                  | 0.795  | -3.38      | -3.38      | -1.82         | 1.56           |             |
| Si     | 3.364  | 2.415                  | 1.181  | -3.30      | -3.30      | -1.84         | 1.46           |             |
| N      | 3.337  | 2.018                  | 0.927  | -3.54      | -3.91      | -2.35         | 1.56           |             |
| P      | 3.348  | 2.446                  | 1.531  | -3.80      | -3.80      | -2.26         | 1.54           |             |
| As     | 3.349  | 2.595                  | 1.749  | -3.86      | -3.86      | -2.30         | 1.56           |             |
| O      | 3.332  | 2.088                  | 1.047  | -3.40      | -3.40      | -1.81         | 1.63           |             |
| S      | 3.346  | 2.436                  | 1.522  | -3.39      | -3.39      | -1.76         | 1.61           |             |
| undoped| 3.351  | 2.570                  | 1.641  | -3.36      | -3.36      | -1.74         | 1.62           |             |
| Te     | 3.358  | 2.762                  | 1.932  | -3.33      | -3.33      | -1.73         | 1.60           |             |
| F      | 3.341  | 2.276                  | 1.253  | -2.52      | -3.94      | -2.28         | 1.66           |             |
| Cl     | 3.353  | 2.534                  | 1.621  | -2.43      | -3.92      | -2.43         | 1.51           |             |
| Br     | 3.358  | 2.673                  | 1.803  | -2.45      | -3.90      | -2.27         | 1.63           |             |
| I      | 3.363  | 2.853                  | 2.037  | -2.48      | -3.87      | -2.26         | 1.61           |             |

Figure 1. (a) Top view and (b) side view of the crystal structure of a $4 \times 4 \times 1$ doped supercell monolayer MoSe$_2$. The blue, yellow and purple spheres denote the Mo, Se and NM atoms, respectively.
where $E_{\text{doped}}$ is the total energy of the monolayer MoSe$_2$ with one Se atom replaced by the NM atom, $E_{\text{vacancy}}$ is the total energy of the monolayer MoSe$_2$ with one Se vacancy, and $\mu_{\text{NM}}$ is the chemical potential of the dopant and is calculated with respect to the elemental bulk or gas in nature. Positive $E_b$ suggests that doped atom is energetically favorable to sit at the substitutional site of Se.

**Figure 2.** The band structures of undoped and NM doped monolayer MoSe$_2$. The light blue and light purple background colors are represent the band structures of the odd and even number valence electrons doped systems, respectively. NM dopants with an even number of valence electrons are generally p-type conductivity. On the contrary, NM dopants with an odd number of valence electrons can provide effective p-type or n-type conductivity.
Results and Discussions

Binding energies and optimized Structures. Table 1 lists the calculated results of the doped systems. All of them (except for B- and C-doped) have positive $E_b$, indicating that their formations are exothermic reaction and therefore stable. The $E_b$ of the VIA (O, S and Te) group doped is the largest ($>2$ eV). This is due to the dopants have the same valence electron structure as Se. Thus they are most stable when fill up the Se vacancy. O-doped system, overall, has the largest $E_b$ (3.78 eV), since O atom has the highest electronegativity. The $E_b$ of the VA (N, P and As) and VIIA (F, Cl, Br and I) group doped are smaller (~1 eV). This is probably due to the absent or extra one electron cost some formation energy. Doping of NM atoms with the IA (H), IIIA (B) and IVA (C and Si) groups is less energetically favorable, with $E_b$ of ~0 eV. This can be attributed to their valence electron structures have the largest difference compared with Se.

Figure 3. The average PDOS of Mo, Se and NM atoms of undoped and NM doped monolayer MoSe₂.
Although their \( E_b \) varies a lot, their lattice structures stay constant, within 0.6%. On the other hand, the local structure and the electronic properties have been modified dramatically. The Mo-NM bond lengths (\( d_{\text{Mo-NM}} \)) and \( h \) (the sheet thicknesses from NM atom to the reference Mo atom plane, Fig. 1(b)) of doped MoSe\(_2\) vary as much as 21.5% and 51.6%, respectively. This is mostly due to the variation of the atomic radius and electronegativity of NM atoms. More details will be discussed later.

**Electronic and electrical transport properties.** To explain how doped NM atoms modify the electronic properties of monolayer MoSe\(_2\), we have calculated the band structures and partial density of states (PDOS) of individual Mo, Se and NM atoms of all the systems, as shown in Figs 2 and 3, respectively. For undoped monolayer MoSe\(_2\), conduction band (CB) and valence band (VB) are composed of Mo-4\(d\) and Se-4\(p\) states, and each Mo atom can provide four electrons interacting with the surrounding six Se atoms. For IVA (C and Si) and VIA (O, S and Te) group doped systems (NM dopants with even number of valence electrons), the Fermi level (\( E_F \)) of doped MoSe\(_2\) is almost unchanged (\(-0.04\) to \(-0.06\) eV, see Table 1) compared to the undoped one and is slightly above the valence band maximum (VBM), seen in Fig. 2. These phenomena are consistent with the results in C-,
Si-, O-, Se- and Te-doped monolayer MoS\textsubscript{2} or WSe\textsubscript{2} and IIIA dopants with an even number of valence electrons doped monolayer MoSe\textsubscript{2} is still generally a p-type semiconductor.

For IIIA (B) and VA (N, P and As) group doped cases, the \(E_F\) lowered about 0.18~0.50 eV compared to the undoped one. The similar results have also been reported in B- N-, P- and As-doped monolayer MoS\textsubscript{2} or WSe\textsubscript{2} and N-, P- and As-doped monolayer MoSe\textsubscript{2}\textsuperscript{21,28,39,40}. Thus, they are still a p-type semiconductor. For IA (H) group doped case, a half-\(\ell\)filled impurity level (mostly composed of Mo-4\(d\) states) appears within the band gap and lifts the \(E_F\) into the middle of the band gap. Thus p-type conductivity is suppressed. For VIIA (F, Cl, Br and I) group doped systems, an additional valence electron results in the donor impurity level (consisting Mo-4\(d\) and NM-\(p\) states) and the \(E_F\) is lifted close to the conduction band minimum (CBM). Thus, they become an n-type semiconductor, consistent with the reported results\textsuperscript{21,28,39,40}. Thus, we can conclude that NM dopants with an odd number of valence electrons doped MoSe\textsubscript{2} can have p-type or n-type conductivity. On the contrary, NM dopants with an even number of valence electrons can only provide p-type conductivity. This suggests a possible way to realize bipolar electrical transport properties by tuning the dopants, which is essential for practical applications in optoelectronics and electronics.

We further observe the PDOS of all doped systems found that Mo-4\(d\) (green lines) and Se-4\(p\) states (red lines) are basically invariable, while the NM-\(p\) (or -\(s\)) states (blue lines) demonstrate huge difference (see Fig. 3). Therefore, we believe that the dopants can only affect the local electronic structure. This is also verified by the calculated electronic density difference. Overall, the dopants only affect the electronic distribution of the three nearest neighboring Mo atoms, other atoms are unaffected. Thus, in Fig. 4, we only demonstrate the electronic density difference of the NM and the closest Mo and Se atoms. The blue (or red) regions indicate the electron loss (or accumulation), and the red regions between the two atoms indicate that they form a covalent bond. Thus, the Se and the Mo atom are ionized; meanwhile, a covalent bond is formed between them in undoped monolayer MoSe\textsubscript{2}. It is found that Mo-NM ionic bonds are formed in the N-, O- and F-doped system, due to their large electronegativity. On the other hand, covalent bonds with different strength are formed for other dopants. Thus we believe the change of the globe electronic properties of the doped MoSe\textsubscript{2} is due to this local change of electron distribution.

**Optical and photocatalytic properties.** We have also calculated the optical properties of all the systems and the results show that NM dopants slightly affect the optical absorption edge and optical absorption areas in the range of 300 to 900 nm (see Supplementary Fig. S1). On the other hand, this work also provides the...
highest occupied molecular state (HOMO) and lowest unoccupied molecular state (LOMO) of all the systems (show in Fig. S2). We have found that the physical location of HOMO and LUMO can be tuned by different NM dopants.

For undoped MoSe$_2$, the HOMO and LUMO are made up of Mo-$4d$ states, thus they are located at all the Mo atoms simultaneously (Fig. S2(k)). And the photogenerated electrons (e$^-$) and holes (h$^+$) will be easily recombined on Mo atoms, which reduce the photocatalytic efficiency. For IVA (C and Si) group doped MoSe$_2$, both the HOMO and LUMO mainly locate at the NM atom and its three nearest Mo atoms. For VIA (O, S, and Te) group doped MoSe$_2$, similar to undoped MoSe$_2$, both the HOMO and LUMO mainly locate at the Mo atoms across the film. Thus, in these two cases, the photogenerated electrons e$^-$/h$^+$ have a good chance to recombine.

For IA (H) group and VIIA (F, Cl, Br, and I) group doped MoSe$_2$, the distribution of HOMO states is the same as the undoped MoSe$_2$, while the LUMO states are mainly located at the NM atom and its three nearest Mo atoms. For IIIA (B) doped MoSe$_2$, the distribution is opposite to them. For VA (N, P, and As) group doped MoSe$_2$, the HOMO states locate at around NM atom and its surrounding Mo atoms, and the LUMO states locate at Mo atoms further away from NM atoms. In these three cases, the HOMO and LUMO states are separated in real space.

O$_2^-$ ion and OH radical are important oxidants for the degradation of organic pollutants. As an example, the schematic mechanism of photocatalytic degrading process is shown in Fig. 5 for VIIA (F, Cl, Br, and I) group doped MoSe$_2$ system. Under light irradiation, the e$^-$ and h$^+$ will be generated at the yellow and purple region, respectively. Next, O$_2^-$ ions and OH radicals can be reduced or oxidized by the e$^-$ or h$^+$, simultaneously. And they can oxidize the organic pollutant into H$_2$O and CO$_2$. Thus, due to the separation of the HOMO and LUMO states in the real space, NM dopants with an odd number of valence electrons doped monolayer MoSe$_2$ can suppress the recombination probability of the photogenerated e$^-$ and h$^+$, and increase the photocatalytic performance.

Further, the VBM and CBM position are calculated relative to the vacuum level. As shown in Fig. 6 and Table 1, the oxidation potential of the photogenerated h$^+$ is enhanced by 0.44–0.64 eV, while the reduction potential of photogenerated e$^-$ is reduced by 0.52–0.69 eV in the NM dopants with odd number of valence electrons (IA, VIIA, VA and VIIA) doped monolayer MoSe$_2$. On the contrary, the NM dopants with even number of valence electrons even (IVA and VIA doped MoSe$_2$) barely changed the redox potential. Thus, NM dopants with odd number of valence electrons can modify the redox potentials, and tends to generate more OH radical than O$_2^-$ ion in the photocatalytic reaction. This is consistent with the experimental report that the OH radical played a dominant role in the visible light photocatalytic degradation of RhB for the B/C-doped TiO$_2$.

Conclusions

In this work, the geometrical structure, electrical transport, redox potentials, molecular state, optical and photocatalytic properties of NM doped monolayer MoSe$_2$ are studied by first principle calculations. The $E_g$ suggests that NM doped MoSe$_2$ are energetically favorable compared to Se vacancies, except B- and C-doped MoSe$_2$. We have found that NM dopants with odd number of valence electrons doped monolayer MoSe$_2$ can be p-type or n-type, while dopants with even valence electrons doped ones tend to be p-type. This provides a useful method to realize bipolar electrical transport properties by tuning the dopants for the applications in optoelectronics and electronics. We have also found NM dopants with odd number of valence electrons doped MoSe$_2$ have better photocatalytic performance, due to they can suppress the recombination of photogenerated e$^-$ and h$^+$, and enhance the oxidation potential of the holes.

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**Author Contributions**

The idea was proposed by Y.F.Z. and L.H. The simulations and data analyses were performed by Y.F.Z., Y.F.Z. wrote the manuscript, C.L. and W.W. prepared the table and the figures. All authors discussed the results and reviewed the manuscript.

**Additional Information**

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