Rh-doped MoSe$_2$ as a toxic gas scavenger: a first-principles study

Hao Cui, Guozhi Zhang, Xiaoxing Zhang, and Ju Tang

Using first-principles theory, we investigated the most stable configuration for the Rh dopant on a MoSe$_2$ monolayer, and the interaction of the Rh-doped MoSe$_2$ (Rh-MoSe$_2$) monolayer with four toxic gases (CO, NO, NO$_2$, and SO$_2$) to exploit the potential application of the Rh-MoSe$_2$ monolayer as a gas sensor or adsorbent. Based on adsorption behavior comparison with other 2D adsorbents and desorption behavior analysis, we assume that the Rh-MoSe$_2$ monolayer is a desirable adsorbent for CO, NO and NO$_2$ storage or removal given the larger adsorption energy ($E_{\text{ad}}$) of $-2.00$, $-2.56$ and $-1.88$ eV, respectively, compared with other materials. In the meanwhile, the Rh-MoSe$_2$ monolayer is a good sensing material for SO$_2$ detection according to its desirable adsorption and desorption behaviors towards the target molecule. Our theoretical calculation would provide a first insight into the TM-doping effect on the structural and electronic properties of the MoSe$_2$ monolayer, and shed light on the application of Rh-MoSe$_2$ for the sensing or disposal of common toxic gases.

1. Introduction

Sensing toxic gases, especially detection of the ones at sub-ppm levels, is quite imperative with respect to environmental standards and agricultural pollution monitoring. In this regard, researchers have always contributed to finding novel sensing materials for potential application as chemical sensors with a rapid response, high sensitivity and low cost. In the past few decades, semiconducting metal oxide nanowire,$^{1-3}$ carbon nanotube,$^{4*, 5}$ and graphene$^{6}$ based sensors have successively caught the attention of researchers, arousing considerable interest from the research community. Nevertheless, they are never satisﬁed by these achievements, persisting to pursue some new materials that possess more fascinating sensing behavior than the previous ones.

After the successful application of graphene as a gas sensor, scholars have turned their attention to two-dimensional (2D) materials that have large surface-volume ratios and tunable electronic properties due to their unique structural configuration. Materials such as hexagonal boron nitride,$^{7}$ antimonene,$^{8}$ phosphorene$^{9}$ and silicene$^{10}$ have become the focus of the sensing field, in order to find candidate materials having the advantages of graphene such as high carrier mobility and strong chemical activity for gas interaction,$^{11-13}$ as well as semiconducting properties. In the meanwhile, group III-V nitrides, particularly AlN and InN,$^{14,15}$ have been regarded as promising structures for gas sensing,$^{16,17}$ and the experimental breakthrough in the synthesis of InN$^{18}$ makes it possible to be used as a substitute for graphene with inherent bandgap characteristics.$^{19}$

Very recently, 2D transition metal dichalcogenides (TMDs), especially MoS$_2$ monolayers,$^{20-22}$ have attracted much attention as alternative materials to conventional metal oxides for chemical sensing devices. Moreover, surface doping with transition metal (TM) atoms has been demonstrated to provide a monolayer with enhanced adsorption and sensing performance for gas molecules due to the improved chemical activity and electron mobility induced by the TM dopant,$^{23}$ opening up a novel insight into the sensor family. Other than that, MoSe$_2$, as a new emerging semiconducting material, has been investigated as well for its application as a sensor. While Late et al. first reported the high sensing performance of the MoSe$_2$ monolayer for ppm-level NH$_3$ gas,$^{24}$ Baek et al. developed a MoSe$_2$ multilayer based field-effect transistor for NO$_2$ detection.$^{25}$ However, the potential applications of MoSe$_2$ based materials need to be further explored and broadened after their successful synthesis by chemical vapor deposition.$^{26}$ This inspires us to implement a first-principles calculation to study the adsorption performance of TM-MoSe$_2$ monolayers towards four industrial exhaust gases including CO, NO, NO$_2$ and SO$_2$ to put forward a novel material for toxic gas sensing. Among numerous TM atoms, rhodium (Rh) is the one with strong electron mobility and catalytic performance for gas interaction, previously demonstrated by carbon nanotube,$^{27}$ graphene,$^{28}$ and MoS$_2$ monolayer systems$^{29}$ where Rh was proposed as a dopant to functionalize the proposed surfaces. We assumed that it
would be interesting and necessary to investigate the adsorption and sensing behaviors of the Rh-doped MoSe$_2$ (Rh-MoSe$_2$) monolayer towards toxic gases to exploit the novel material for toxic gas detection or removal. The results indicate that the Rh-MoSe$_2$ monolayer possesses quite strong adsorption behavior towards CO, NO and NO$_2$ molecules that give rise to chemisorption in these systems, while physisorption could be determined for the Rh-MoSe$_2$/SO$_2$ system. Through adsorption behavior comparison with other 2D adsorbents and desorption behavior analysis, we assume that Rh-MoSe$_2$ is a desirable adsorbent for CO, NO and NO$_2$ storage or removal while being a good sensing material for SO$_2$ detection. To the best of our knowledge, this would be the first report investigating the potential application of Rh-MoSe$_2$ for the removal of four toxic species in a theoretical manner.

2. Computational details

In this work, spin-polarized calculations were implemented in the Dmol$^3$ package$^{26}$ of Materials Studio. The Perdew–Burke–Ernzerhof (PBE) functional with a generalized gradient approximation (GGA) was employed to deal with the electron exchange and correlation,$^{37}$ and to obtain the optimized structures. The Grimme method was employed$^{38}$ for better understanding the van der Waals interaction. We selected double numerical plus polarization (DNP) as the atomic orbital basis set,$^{26}$ while the DFT semi-core pseudopotential (DSSP) method was employed to dissolve the relativistic effect of the TM atom.$^{39}$ The $k$-point sample of the Monkhorst–Pack grid was sampled to $5 \times 5 \times 1$ of the Brillouin zone for geometry optimization and to $7 \times 7 \times 1$ for electronic structure calculations.$^{40}$ The energy tolerance accuracy, maximum force, and displacement were selected as $10^{-5}$ Ha, $2 \times 10^{-3}$ Ha Å$^{-1}$, and $5 \times 10^{-3}$ Å,$^{11}$ respectively. For static electronic structure calculations, a self-consistent loop energy of $10^{-6}$ Ha, global orbital cut-off radius of 5.0 Å and smearing of 0.005 Ha were employed to ensure the accurate results of total energy.$^{41}$ For basis set superposition errors (BSSE), little impact could be caused in the Dmol$^3$ package,$^{42}$ and thus we would not analyze it in the following part.

A $4 \times 4 \times 1$ MoSe$_2$ monolayer supercell including 16 Mo and 32 Se atoms with a vacuum region of 15 Å was established and relaxed to its most stable configuration. A previous report has proved that a $4 \times 4$ supercell would be large enough to conduct the gas adsorption process while a 15 Å slab would be appropriate to prevent the interaction between adjacent units.$^{43}$ The lattice constant calculated here was 3.30 Å, which is in agreement with other theoretical studies (3.31 Å (ref. 45)).

The adsorption energy ($E_{ad}$) of each gas adsorption process was calculated by the following equation:$^{24}$

$$E_{ad} = E_{Rh-MoSe_2/gas} - E_{Rh-MoSe_2} - E_{gas}$$  \hspace{1cm} (1)

where the $E_{Rh-MoSe_2/gas}$, $E_{Rh-MoSe_2}$, and $E_{gas}$ represent energies of the adsorbed system, isolated Rh-MoSe$_2$ and gas molecule, respectively. To analyze the charge transfer ($Q_{T}$) between the target molecule and adsorbent surface, the Mulliken population analysis was considered, characterized by the carried electron value by gas molecules after adsorption. Only the most favorable configuration for gas adsorption would be plotted and analyzed in the following parts.

3. Results and discussion

3.1 Geometric and electronic structure of Rh-MoSe$_2$

We determined Rh atom adsorption onto a bare MoSe$_2$ monolayer Rh-MoSe$_2$, where four possible sites were considered, traced as $T_{Mo}$ (above the center of the hexagonal ring of MoSe$_2$), $T_{Se}$ (at the top of the Se atom) and $B_{Mo,Se}$ (the bridge site between two Se atoms), respectively. The binding energy ($E_b$) for Rh adsorption onto the most favorable binding site is determined through the formula:

$$E_b = E_{Rh-MoSe_2} - E_{Rh} - E_{MoSe_2}$$  \hspace{1cm} (2)

where $E_{Rh-MoSe_2}$, $E_{Rh}$, and $E_{MoSe_2}$ represent the energies of the Rh-MoSe$_2$, Rh atom and pure MoSe$_2$, respectively.

After optimization, the most stable configuration of Rh-MoSe$_2$ in line with relevant deformation charge density (DCD) is shown in Fig. 1. One can see that the Rh atom tends to be adsorbed onto the MoSe$_2$ monolayer through the $T_{Mo}$ site, with three Rh–Se bond lengths of 2.383, 2.383 and 2.354 Å, respectively. The geometry of MoSe$_2$ undergoes a little deformation after Rh doping due to the binding force of Rh–Se bonds.$^{43}$ The $Q_{T}$ between the Rh dopant and the MoSe$_2$ monolayer is found to be $-0.239$ e, indicating that the Rh dopant acts as an electron acceptor while the MoSe$_2$ monolayer acts as a donor. This is in line with the strong electron withdrawing properties of the Rh atom,$^{44}$ thereby leading to high electron localization around the Rh atom. In addition, we can find that the Mo atoms are mainly the electron accepting centers while the Se atoms are the electron donating centers for the optimized Rh-MoSe$_2$ system.

![Fig. 1 Geometric structures (a) and (b) and DCD (c) of the Rh-MoSe$_2$ monolayer. The black values are the atom-to-atom distance while the red value is the electron amount carried by Rh dopant.](image-url)
To further elucidate the electronic behavior of the Rh doping effect on the MoSe₂ monolayer compared with its pure counterpart, density of states (DOS) analysis is performed, as depicted in Fig. 2. It can be seen in the total DOS distribution of Fig. 2(a) that there is a big band gap near the Fermi level in the DOS curve of intrinsic MoSe₂, confirming its semiconducting properties well. With the doping of the Rh atom, the gap gets narrowed obviously due to the upward shifted Fermi level which was originally identified as the valence band maximum in the Dmol³ package, caused by the Rh contribution. It is interesting to note that the DOS spin up and down of the Rh-MoSe₂ monolayer are shown to be asymmetric in comparison with those in the pure MoSe₂ system that shows good symmetry, which could be ascribed to the total magnetic moment of 1.0 µB in this system induced by the Rh dopant. Moreover, due to the electron-donating behavior of the MoSe₂ monolayer that results in an improved effective coulombic potential, the DOS curve of the Rh-MoSe₂ system is found to left shift towards a lower region consequently compared with that of its intrinsic counterpart. In Fig. 1(b), the DOS of the Rh 4d orbital is largely overlapped with that of the Se 4p orbital, demonstrating strong hybridization of the Rh atom onto the MoSe₂ monolayer. Apart from that, it reveals that the highest occupied molecular orbitals (HOMOs) are mainly located at the Se atom while the lowest unoccupied molecular orbitals are at the Rh atom, which confirms the results of DCD that charge is accumulated around the Rh dopant.

3.2 CO adsorption

Fig. 3 shows the most stable configuration and related DCD for CO adsorption on the Rh-MoSe₂ monolayer. One can see that the C atom is trapped by the Rh dopant with a Rh–C bond length of 1.892 Å after the CO molecule is adsorbed on the surface. It would be worth noting that such a value of atom-to-atom distance is even shorter than the sum of the corresponding covalent radii (2.00 Å for Rh–C) indicating some chemisorption in this system. In fact, the large enough E_{ad} of ~2.00 eV here could not only confirm the strong adsorption performance of Rh-MoSe₂ towards the CO molecule, but also indicate its chemical nature with strong spontaneity for this interaction. In the meanwhile, three Rh–Se bonds, after CO adsorption, are elongated to 2.432, 2.448 and 2.399 Å, respectively, and the C–O bond of the CO molecule is prolonged to 1.164 Å from 1.142 Å in an isolated molecule. These findings suggest the activation behavior for the CO molecule when interacted with the...
monolayer. The DCD shows that the Rh-MoSe₂ monolayer acting as an electron acceptor withdraws 0.131 e from the adsorbed CO molecule. This, combined with the Mulliken population analysis for the Rh dopant that carries 0.467 e after adsorption, indicates that the Rh dopant is an electron localization center accepting charge from both gas molecules and the MoSe₂ surface.

Fig. 4 shows the total and partial DOS distributions for the CO adsorption system. Based on the comparison between the total DOS for the pure Rh-MoSe₂ system and the one for the adsorbed system, we can find that they are basically overlapped except for the area near the Fermi levels where the Rh dopant contributes a lot due to its strong electron activity, and the areas at 6.5 and 8.5 eV where the adsorbed CO molecule makes a great contribution for the DOS of the whole system. Besides, the deformations for the DOS between the isolated CO molecule and the adsorbed one confirm that the CO molecule is activated during gas adsorption. Moreover, the large overlaps between DOS of Rh 4d and C 2p orbitals manifest strong hybridization between Rh and C atoms, which would explain the strong binding force of the Rh–C bond that leads to the short atom-to-atom distance.

3.3 NO adsorption

The most stable adsorption configuration and related DCD for the Rh-MoSe₂/NO system are exhibited in Fig. 5. One can observe that the structure for NO adsorption onto the Rh-MoSe₂ monolayer, with N atoms captured, is somewhat similar to that of the CO system. However, the largely elongated Rh–Se bonds with lengths of 2.445, 2.453 and 2.449 Å in the NO system suggest a stronger binding force of Rh on the NO molecule than the CO molecule. Similarly, the elongated N–O bond of 1.178 Å in the adsorbed NO molecule in comparison with its isolated counterpart (1.164 Å) indicates the activation behavior of the NO molecule for interaction with the Rh-MoSe₂ monolayer. The shorter length of the Rh–N bond (1.911 Å) compared with the sum of relevant covalent radii (1.96 Å for Rh–N⁴⁹) shows the nature of chemisorption. In fact, all these results could be well supported by the large $E_{ad}$ of $\sim 2.56$ eV and $Q_T$ of $\sim 0.322$ e calculated in this system as they are large enough to confirm the strong interaction between gas molecules and the adsorbent surface.⁵¹

From the DOS distribution for the NO system as portrayed in Fig. 6, the electronic behavior for NO adsorption on the Rh-MoSe₂ monolayer could be elucidated clearly. In the total DOS distribution, we can see that the DOS of the NO system transforms slightly above the Fermi level compared with that of the pure Rh-MoSe₂ system. In detail, two novel peaks appear at around $-7.5$ and $-8.5$ eV while one peak at the Fermi level disappears after gas adsorption, which could be attributed to the DOS deformation of the adsorbed NO molecule. It could be seen that the DOS peak of the isolated NO molecule at the Fermi level splits into two small peaks after NO adsorption that weakens the contribution to the total DOS of the whole system, while the slightly weakened peak at $-8.5$ eV and the enhanced peak at $-7.5$ eV accord with the novel peaks in DOS for the adsorbed system. Based on the partial DOS analysis, we could see that every peak of the N 2p orbital is overlapped with that of the Rh 4d orbital, implying that the N atom is strongly hybridized with the Rh dopant, thus giving rise to a strong binding force for the Rh–N bond.

3.4 NO₂ adsorption

In terms of NO₂ adsorption onto the Rh-MoSe₂ monolayer, one can see from Fig. 7 that the NO₂ molecule prefers to adsorb two
O atoms trapped with a shorter Rh–O distance of 2.113 Å. Three Rh–Se bonds of Rh-MoSe₂ in line with the N–O bond of the NO₂ molecule undergo some elongation after adsorption, due to the binding force of Rh on the NO₂ molecule. The Mulliken population analysis indicates that 0.361 e transfers from the Rh-MoSe₂ monolayer to the NO₂ molecule with an electron loss of 0.086 for the Rh dopant. That is to say, unlike in the CO system, the Rh dopant acts as an electron donor releasing the electron to the gas molecule, which could be found in NO and SO₂ systems as well. This finding manifests the strong electron mobility and chemical activity of TM when interacting with gas molecules. Moreover, the large Qₐ associated with the relatively large Eᵤₐ suggests the kind of chemisorption for the Rh-MoSe₂/NO₂ system.

Fig. 8 shows the DOS distributions for the NO₂ adsorption system. One can find from the total DOS configurations that the DOS curve transforms dramatically around the Fermi level after adsorption of the NO₂ molecule. This may be attributed to the considerable electron-transfer between gas molecules and the adsorbent surface that results in electron redistribution for the whole system, thus leading to the deformation of electronic states at the Fermi level. Furthermore, the novel emerged peaks at −7.5, −8.5 and −11.5 eV are contributed by the adsorbed NO₂ molecule which is activated during adsorption. Similarly, the hybridization between Rh and O atoms is identified through the phenomenon of overlaps between Rh 4d and O 2p orbitals.

3.5 SO₂ adsorption

From Fig. 9 where the most stable configuration for SO₂ adsorption on the Rh-MoSe₂ monolayer is displayed, we can see that, similar to the NO₂ adsorption configuration, the SO₂ molecule is adsorbed on the Rh-MoSe₂ monolayer with two O atoms oriented. However, the SO₂ molecule here stands a little far from the Rh dopant, with the nearest atom-to-atom distance measured to be 2.275 Å, which indicates a weak interaction in
the Rh-MoSe$_2$/SO$_2$ system. The tiny prolongation for Rh–Se bonds inner Rh-MoSe$_2$ to 2.423, 2.404 and 2.392 Å by 0.019 Å can confirm the weak binding force between the Rh dopant and the SO$_2$ molecule as well. The $E_{\text{ad}}$ obtained here is $-0.89$ eV and the Mulliken population analysis shows a $Q_T$ of 0.285 e from the Rh-MoSe$_2$ monolayer to the SO$_2$ molecule. All these findings suggest physisorption for SO$_2$ adsorption on the Rh-MoSe$_2$ monolayer.

3.6 Application of Rh-MoSe$_2$ to toxic gas scavenging

We first investigated the potential application of Rh-MoSe$_2$ as a resistance-type sensor for these gases. According to our previous analysis, it could be found that the Rh-MoSe$_2$ monolayer has quite strong adsorption performance for three species namely CO, NO and NO$_2$ molecules, giving rise to chemisorption in these systems, while having relatively weaker performance towards SO$_2$ adsorption that gives rise to physisorption instead. In other words, it would be difficult for these three gas molecules to desorb from the Rh-MoSe$_2$ monolayer once they are adsorbed onto the surface, except for the SO$_2$ molecule which may be desorbed through annealing at high temperature or irradiation with ultraviolet light.$^{56,57}$

To confirm this assumption, the recovery time ($\tau$) analysis based on transition state theory and van’t-Hoff–Arrhenius expression$^{55}$ was implemented, and expressed as:

$$\tau = \frac{A}{E_{\text{ad}}} e^{(-E_{\text{ad}}/K_B T)} \quad (3)$$

where $A$ is the attempt frequency determined as $10^{12}$ s$^{-1}$ according to a previous report,$^{56}$ $T$ is the temperature and $K_B$ is the Boltzmann constant ($8.318 \times 10^{-3}$ kJ (mol K)$^{-1}$). Given the inverse processes between adsorption and desorption, we assume the value of $E_{\text{ad}}$ as the potential barrier ($E_a$) for desorption. It would be obvious that a larger $E_{\text{ad}}$ would lead to a harder process for gas desorption, and the increase of temperature can accelerate that process effectively. According to the obtained $E_{\text{ad}}$ in our calculations as shown in Table 1, we plotted the recovery time for the desorption of various gases at various temperatures as portrayed in Fig. 11. One can conclude that CO, NO and NO$_2$ desorption from the Rh-MoSe$_2$ monolayer would be extremely unrealistic at room temperature, and even at 798 K, it would take more than 4 hours for NO desorption from the surface. Although remarkably enhanced behavior for CO and NO$_2$ desorption could be achieved at 798 K, the considerable heat loss and the safety of the devices would be another issue. Therefore, it would be inappropriate to use the Rh-MoSe$_2$ monolayer as the sensing material for CO, NO or NO$_2$ detection, because the one-off operation for gas sensors would be a waste of money and reduce work-efficiency. On the other hand, we assume that Rh-MoSe$_2$ is suitable for SO$_2$ sensing given its good adsorption performance for detection and desorption performance with appropriate recovery time at ambient temperature for recycle use. Moreover, the sensing mechanism of the Rh-MoSe$_2$ monolayer towards SO$_2$ would be dependent on the increased conductivity due to the narrowed energy gap from 1.033 eV for the isolated Rh-MoSe$_2$ monolayer to 0.227 eV for the SO$_2$ system$^{57}$ as seen in Table 1.

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Fig. 9 Adsorption configuration (a) and (b) and DCD (c) of the Rh-MoSe$_2$/SO$_2$ system.

Fig. 10 DOS distribution of the Rh-MoSe$_2$/SO$_2$ system. The dashed line is the Fermi level.

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Second, the large $E_{ad}$ in CO, NO and NO$_2$ systems allows the excellent performance of Rh-MoSe$_2$ as a gas adsorbent for their storage or removal from specific environments. For this purpose, we summarize in Fig. 12 the calculated $E_{ad}$ values of recently reported 2D adsorbents for four gases, in order to find out whether Rh-MoSe$_2$ could be an alternative for scavenging toxic gases. From the figure, we can find that the Rh-MoSe$_2$ monolayer possesses better adsorption performance for CO, NO and NO$_2$ molecules compared with the pure MoS$_2$ monolayer, the pure MoSe$_2$ monolayer, the pure InN, the pure C$_3$N, pure penta-graphene, and some other TM-doped MoS$_2$ monolayers. That is to say, the Rh-MoSe$_2$ monolayer has strong potential to be an adsorbent candidate for CO, NO and NO$_2$ storage and removal. Conversely, it is not a desirable SO$_2$ adsorbent due to its weaker performance than pure InN, penta-graphene, the Au-MoS$_2$ monolayer, the Pt-MoS$_2$ monolayer and the Ni-MoS$_2$ monolayer, although it has better performance than the pure MoS$_2$ monolayer, the pure MoSe$_2$ monolayer and pure C$_3$N, except for the Cu-MoS$_2$ monolayer which is not studied for SO$_2$ adsorption in ref. 22 and 61. In addition, we would introduce the application of borophene as a potential SO$_2$ adsorbent given its strong ability and capacity whereby up to seven SO$_2$ molecules could be chemisorbed on its one side, with a weight percentage of 82.88%, for SO$_2$ adsorption.

<table>
<thead>
<tr>
<th>Gas systems</th>
<th>$E_{ad}$ (eV)</th>
<th>$D$ (Å)</th>
<th>$Q_T$ (e)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>$-2.00$</td>
<td>1.892</td>
<td>$-0.131$</td>
<td>0.202</td>
</tr>
<tr>
<td>NO</td>
<td>$-2.56$</td>
<td>1.911</td>
<td>0.322</td>
<td>1.210</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>$-1.88$</td>
<td>2.113</td>
<td>$-0.361$</td>
<td>0.520</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>$-0.89$</td>
<td>2.275</td>
<td>0.285</td>
<td>0.227</td>
</tr>
</tbody>
</table>

Fig. 11 Recovery time for four species at various temperatures.

4. Conclusions

In this work, we implemented a first-principles theory to study the adsorption performance of the Rh-MoSe$_2$ monolayer towards four toxic gases, including CO, NO, NO$_2$ and SO$_2$. Desorption behavior analysis and adsorption behavior comparison with other 2D materials towards these four species were conducted in order to exploit the potential application of our proposed monolayer. The results indicated that the Rh-MoSe$_2$ monolayer possesses quite strong adsorption behavior towards CO, NO and NO$_2$ molecules that gives rise to chemisorption in these systems, while physisorption could be determined for the Rh-MoSe$_2$/SO$_2$ system. In that regard, based on the adsorption behavior comparison with other adsorbents and desorption behavior analysis, we assume that Rh-MoSe$_2$ is a desirable adsorbent for CO, NO and NO$_2$ storage or removal while it is a good sensing material for SO$_2$ detection. Our theoretical calculation would provide a first insight into the TM-doping effect on the structural and electronic properties of the MoSe$_2$ monolayer, and shed light on the application of Rh-MoSe$_2$ for the sensing or disposal of common toxic gases.

Author contributions

Xiaoxing Zhang conceived and designed the research, Hao Cui performed the research and wrote this manuscript while Guozhi Zhang and Ju Tang helped analyze the data.

Conflicts of interest

There are no conflicts to declare.

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