Research Article
Adsorption Mechanism of Cu-Doped SnO\(_2\) (110) Surface toward H\(_2\) Dissolved in Power Transformer

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The content of hydrogen is a key quantity in condition assessment and fault diagnosis of power transformer. Based on the density functional theory (DFT), the adsorption mechanism of Cu-doped SnO\(_2\) surface toward H\(_2\) has been systematically studied in this work. Firstly, the relaxation, the bond length, and overlap population of both the pure and Cu-doped SnO\(_2\) are computed. To determine the optimal doping position, the formation energies of four potential sites (i.e., Sn\(_5\)-c, Sn\(_6\)-c, Sn\(_5\)-c-s, and Sn\(_6\)-c-s) are then compared with each other. The adsorption energy and the electronic structure of SnO\(_2\) surface are analysed and discussed in detail. Furthermore, to estimate the partial atomic charges and the electrical conductance, the Mulliken population analysis is also performed. It has been found that the bridge oxygen is the most favourable position. The partial density of states of H\(_2\) after adsorption is broadened and shifted close to the Fermi level. A large amount of charges would be transferred and then released back into its conduction band, leading to the reduction of resistance and the enhancement of sensitivity toward H\(_2\). The results of this work provide references for SnO\(_2\)-based sensor design.

1. Introduction

Power transformers are continuously subject to thermal and electrical stresses during the long-term operation. A local overheating or partial discharge would lead to the decomposition of the insulating oil of transformer into gases, including H\(_2\), CH\(_4\), C\(_2\)H\(_4\), C\(_2\)H\(_6\), C\(_2\)H\(_2\), and CO\(_2\) [1]. Compared with other feature gases, the hydrogen is readily separated from dissolved oil and its molecular is the smallest [2–5]. Hence, most of existing online monitoring devices are based on the detection of H\(_2\) [6, 7], and its content is then utilized to assess the condition and diagnose the fault of power transformers.

Presently, a number of sensors have been developed to detect the presence of hydrogen, including the resistive [8–11], the optical fiber [12], the thermoelectric [13], and the surface acoustic wave sensors [14]. Amongst them, the metal oxide semiconductor of SnO\(_2\) is the most employed agent as gas sensor due to its attractive features, such as low cost, small power consumption, and simple structure [15–19]. It has already been applied to air-quality detection, inflammable-gas inspection, environmental monitoring, and so on. However, the pure SnO\(_2\)-based gas sensors suffer from the low sensitivity, the slow response, the lack of selectivity, and aging [6, 20–22].

The doping can significantly modify the geometry and the electronic structure of sensor surface. It is one of the most effective methods to improve the gas sensing properties [23, 24]. Various dopants, for example, Pt, Ag, In, Cr, Pd, Ru, and Cu, are often compounded with SnO\(_2\) to detect specific gases. For instance, Jin et al. [25] investigated the sensing properties of Cu-doped SnO\(_2\) of nanofiber structure mainly towards acetone. The results demonstrated that 2.5 wt% Cu exhibited a low optimum operating temperature and displayed the maximum response and selectivity to acetone. The effects of In, Pd, and Pt on CO adsorption have been studied in [26, 27]. Based on the density functional theory (DFT), the interaction between gas and SnO\(_2\) surface on the atomic scale has been studied by means of the first principle calculations. The results indicated that the doping induces some new electronic states in the band gap, leading to the changes of SnO\(_2\) surface properties. In addition, the X-ray diffraction, scanning electron microscopy, and transmission
electron microscopy are increasingly employed to determine the morphology and structure after doping.

Cu is commonly used as a dopant in SnO$_2$ to improve the sensitivity for detecting hydrogen. It plays an important role in the formation of surface oxygen vacancies in SnO$_2$. The doping of Cu would inevitably change the bond length, the overlap population, and the electronic structure. Several researchers simply synthesized the Cu-doped SnO$_2$ sensor using the sol-gel method and then experimentally investigated its gas sensing performance. Despite considerable effort on this subject, the theoretical analysis is still lacking. The mechanism of the doping on the sensitivity toward H$_2$ is still not well understood and that is the main concern of our work.

The main contribution and the structure of this work are outlined as follows.

(i) The basic structure of SnO$_2$ surface and the hydrogen adsorption models on potential characteristic atoms have been briefly introduced in Section 2, followed by the description of the computing method.

(ii) Based on the DFT, a series of first principle calculations have been performed on the relaxation, the bond length, and the overlap population of SnO$_2$ surface. To determine the optimal doping position, the formation energy is then computed, as presented in Section 3.1.

(iii) Section 3.2 is mainly devoted to the adsorption properties. To gain an insight into the interaction between H$_2$ and SnO$_2$ surface after doping, the adsorption energy is firstly computed. Then, the electronic structure of SnO$_2$ surface is analysed. The Mulliken population analysis is performed to estimate the partial atomic charges and the electrical conductance after Cu doping.

(iv) Finally, the conclusion is addressed in Section 4.

2. Models and Computing Method

2.1. Structure of Stoichiometric SnO$_2$ (110) Supercell. The bulk of SnO$_2$ has rutile tetragonal structure and the primitive cell of SnO$_2$ is composed of 2 Sn atoms and 4 O atoms with experimental lattice parameter $a = b = 4.737 \text{ Å}, c = 3.186 \text{ Å}$. In order to minimize the total energy of the unit cell, the geometry optimization for bulk SnO$_2$ was performed to relax the ions. The calculated lattice constants are $a = b = 4.699 \text{ Å}$ and $c = 3.164 \text{ Å}$, which were lower than the experimental values by 0.8 and 0.7%, respectively.

Since the SnO$_2$ (110) surface is of the lowest energy and the most stable thermodynamic structure among SnO$_2$ [26–30], it is often regarded as a template in the study of doping. Previous research [29] indicates that $2 \times 1$ super cell was suitable to simulate the doping system. When the size of the cell is increased from $2 \times 1$ to $2 \times 2$, much more computational time would be required. Nevertheless, the formation energy and the charge transfer would not be obviously changed. Hence, it is employed in this work and its structure is illustrated in Figure 1(a).

The surface is cleaved from the optimized bulk of SnO$_2$, which is represented by a nine-layer slab. Four layers of the slab contain both Sn and O atoms whereas others contain O atoms only. The SnO$_2$ stoichiometric surface essentially consists of 16 Sn atoms and 32 O atoms, the thickness of which is 13.3 Å, keeping the composition of the primitive cell. There are four kinds of characteristic atoms in the surface, that is, the fivefold coordinated Sn atoms (Sn$_{5c}$), the sixfold coordinated Sn atom (Sn$_{6c}$), the bridge oxygen (O$_{2c}$), and the plane oxygen atom (O$_{3c}$). The doping, as shown in Figure 1(b), is performed by substituting a Sn atom with Cu. In our work, four potential coordinated Sn atoms are considered. Before the surface relaxation, the atoms on the top four layers are allowed to relax in all directions whereas others are fixed.

2.2. Structure of Cu-Doped SnO$_2$ (110) Supercell with H$_2$ Adsorption. Based on the slab model, the adsorptions of H$_2$ on both the pure and Cu-doped SnO$_2$ surfaces are studied. The adsorption site perpendicular to the surface is the favoured site from the perspective of energy [31]. Thus, the molecular of H$_2$ is vertically located on the characteristic atoms and the distance is set to 2 Å, as shown in Figure 2. Referring to [29], the bond length of free H$_2$ molecule is set to 0.74 Å and the size of the periodic cell is $10 \times 10 \times 10 \text{ Å}$. The geometric structure optimization and adsorption energy calculation are then conducted. During the optimization, the adsorbate and the atoms on the top four layers of the surface are relaxed fully.

2.3. Computing Method. The calculations are performed using the software package CASTEP, which employs a plane-wave basis and periodic super cell method based on the DFT theory. The exchange-correction interactions are treated by local density approximation (LDA) method with the Ceperley-Alder-Perdew-Zunger (CA-PZ) function proposed in [32, 33]. Since LDA method underestimates the band gap [29], LDA+U method has been applied through this paper, where U is set to 3.5 eV to optimize the unit cell of bulk rutile SnO$_2$. Meanwhile, the ultrasoft pseudo potentials plane-wave basis is employed; the k-points are set to $4 \times 4 \times 1$ to sample Brillouin zone. To guarantee the convergence, the cut-off energy is set to 400 eV. Note that all the calculations are conducted after the optimization, and the vacuum slab is added upon the surface, the thickness of which is set to 16 Å to prevent interactions between periodic images.

3. Results and Discussion

3.1. Properties of Surface

3.1.1. Geometry Structure. To determine the displacement of outmost layer in the relaxed SnO$_2$ surface relative to their bulk positions, the relaxation of SnO$_2$ surface is firstly computed, as listed in Table 1.

Clearly, all the outmost atoms have deformed to some extent. The characteristic atoms of O$_{2c}$, O$_{3c}$, and Sn$_{6c}$ are shifted along the positive direction of z-axis, and they have moved out of the surface with respect to the bulk termination position by 0.08 Å, 0.10 Å, and 0.20 Å (pure SnO$_2$ surface), respectively. In contrast, the characteristic atom of Sn$_{5c}$ is
Figure 1: Structure of $2\times1\text{SnO}_2$ (110) super cell. (a) Undoped $\text{SnO}_2$ (110) surface; (b) Cu-doped $\text{SnO}_2$ (110) surface; (c) top view of undoped $\text{SnO}_2$ (110) surface; (d) top view of Cu-doped $\text{SnO}_2$ (110). $\text{Sn}_{5c}$ is substituted by Cu.

Figure 2: $\text{H}_2$ adsorption on Cu-doped $\text{SnO}_2$ (110) surface. (a) $\text{H}_2$ adsorbed on $\text{O}_{2c}$. (b) $\text{H}_2$ adsorbed on $\text{O}_{3c}$. The distance is set to 2 Å.
Table 1: Displacement of characteristic atoms along (110) direction.

<table>
<thead>
<tr>
<th></th>
<th>O_{2c}</th>
<th>O_{3c}</th>
<th>Sn_{5c}</th>
<th>Sn_{6c}</th>
<th>Cu_{bc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-doped</td>
<td>0.01</td>
<td>0.10</td>
<td>-0.12</td>
<td>0.05</td>
<td>-0.1</td>
</tr>
<tr>
<td>Pure</td>
<td>0.08</td>
<td>0.10</td>
<td>-0.11</td>
<td>0.20</td>
<td>—</td>
</tr>
<tr>
<td>Reference [34]</td>
<td>0.11</td>
<td>0.20</td>
<td>-0.09</td>
<td>0.23</td>
<td>—</td>
</tr>
<tr>
<td>Reference [35]</td>
<td>0.06</td>
<td>0.18</td>
<td>-0.10</td>
<td>0.20</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 2: Bond length and overlap population of pure and Cu-doped SnO\(_2\) surfaces.

<table>
<thead>
<tr>
<th></th>
<th>Pure SnO(_2) surface</th>
<th>Cu-doped SnO(_2) surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BL (Å)</td>
<td>OP</td>
</tr>
<tr>
<td>O12-Sn12</td>
<td>2.013</td>
<td>0.41</td>
</tr>
<tr>
<td>O12-Cu</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O12-Sn4</td>
<td>2.013</td>
<td>0.41</td>
</tr>
<tr>
<td>O8-Sn8</td>
<td>2.099</td>
<td>0.24</td>
</tr>
<tr>
<td>O12-Sn8</td>
<td>2.099</td>
<td>0.24</td>
</tr>
<tr>
<td>O24-Sn8</td>
<td>2.013</td>
<td>0.41</td>
</tr>
<tr>
<td>O8-Sn15</td>
<td>1.968</td>
<td>0.52</td>
</tr>
<tr>
<td>O24-Sn15</td>
<td>1.968</td>
<td>0.52</td>
</tr>
<tr>
<td>O28-Sn15</td>
<td>2.099</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Notes: the bond length and overlap population of Cu-SnO\(_2\)-O16, Cu(Sn12)-O28, and Cu(Sn12)-O32 are the same with Cu(Sn12)-O12.

Table 3: Formation energy of Cu-doped SnO\(_2\) surface (unit, eV).

<table>
<thead>
<tr>
<th></th>
<th>Sn_{5c}</th>
<th>Sn_{6c}</th>
<th>Sn_{5c,d}</th>
<th>Sn_{6c,d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doping formation energy</td>
<td>3.47</td>
<td>4.11</td>
<td>4.67</td>
<td>4.55</td>
</tr>
</tbody>
</table>

The doping of Cu in SnO\(_2\) is achieved through substituting a Sn atom by a Cu atom in the slab model. Four potential sites are considered in our work, that is, Sn_{5c}, Sn_{6c}, Sn_{5c,d}, and Sn_{6c,d} (see Figure 1). The formation energy is defined as [26]

\[
E_{\text{form}} = E_{\text{total}}(\text{Cu-doped}) - E_{\text{total}}(\text{pure}) + \mu_{\text{Sn}} - \mu_{\text{Cu}} - \mu_{\text{e}} \tag{1}
\]

where \(E_{\text{total}}(\text{Cu-doped})\) is the total energy of Cu-doped SnO\(_2\) surface supercell, \(E_{\text{total}}(\text{pure})\) is the total energy of pure SnO\(_2\) surface supercell, and \(\mu_{\text{Sn}}\) and \(\mu_{\text{Cu}}\) are the energy of Sn and Cu atoms in their bulk crystals, respectively. The results of the doping formation energy are listed in Table 3.

Compared with the atoms of Sn_{5c} and Sn_{6c} in the second layer, the doping formation energy is relatively smaller when occurring on the top layer. Correspondingly, the structure is more stable. Among these four coordination atom positions, the formation energy is the smallest when Sn_{5c} is removed by Cu, which indicates the most stable doping form. Hence, the studies on H\(_2\) adsorption presented below are based on this model.

3.1.2. Electronic Structure. The total density of states (TDOS) of Cu-doped SnO\(_2\) surface and the partial density of states (PDOS) of O, Sn, and Cu atoms are depicted in Figures 3 and 4, respectively.

The PDOS of SnO\(_2\) is mainly composed of the valence band and the conduction band. The valence band can be further divided into the lower part and the upper part. It can be seen that the lower part is distributed from -20.5 eV to -15.1 eV, which are mainly from O2s\(^2\) electron orbital composition and partly from Sn5s\(^2\), 5p\(^2\), and Cu3d\(^{10}\), and 4s\(^1\) electron orbital composition. In contrast, the upper part is distributed from -9.76 eV to 0.79 eV, which are mainly from O2p\(^4\), Sn5s\(^2\), 5p\(^2\), Cu3d\(^{10}\), and 4s\(^1\) electron orbital composition. In terms of the conduction band, it is distributed from 1.68 eV to 9.21 eV, which are mainly from Sn5s\(^2\) and Sn5p\(^3\) electron orbital composition and partly from O2s\(^2\) and O2p\(^4\) electron orbital composition.

Compared with pure SnO\(_2\) surface, the valence band is slightly increased after doping. However, the conduction band is drastically changed. The Fermi level, which refers to zero energy, is shifted towards higher energy but the conduction band is moved to lower energy area. The band structure analysis shows that the band gap is narrowed from 1.68 eV to 9.21 eV. Such result agrees well with that reported in [36] but smaller than the experimental value (the band gap of pure SnO\(_2\) is 3.6 eV). The difference is due to the LDA method. It underestimates the binding energy of the d states of Sn, which has a great impact on the band gap [29]. Meanwhile, the electron orbital of Cu3d\(^{10}\) was injected into the band gap. The additional electronic states introduced by doping can accelerate the migration of carriers effectively between the bands.
3.2. Adsorption Properties

3.2.1. Adsorption Energy. The adsorption energy is a key quantity in evaluating the adhesive property of the system. The energy, which is defined as the reversible energy required to separate an adsorption system into a clean surface and an adsorbed molecular, can be expressed by

$$\Delta E_{\text{ads}} (H_2) = E(\text{SnO}_2) + E(H_2) - E_{\text{total}} (H_2 + \text{SnO}_2),$$

(2)

where $E(\text{SnO}_2)$ and $E(H_2)$ represent the energy of pure SnO$_2$ surface and free H$_2$, respectively. $E_{\text{total}} (H_2 + \text{SnO}_2)$ represent the total energy of adsorption model after geometry optimization. The adsorption energy of both Cu-doped and pure SnO$_2$ surface is listed in Table 4.

If the adsorption energy is positive, it is an exothermic reaction and the process is spontaneous. Otherwise, the system is energetically instable and the reaction is thermodynamically disfavoured. Generally, the larger the energy, the stronger the gas adsorption.

In terms of pure SnO$_2$ surface, the adsorption energies of H$_2$ adsorbed on O$_{3c}$, Sn$_{5c}$ is negative, which means that O$_{3c}$ and Sn$_{5c}$ are energetically unfavourable adsorption sites. In the case of O$_{2c}$, Sn$_{6c}$, and Cu$_{5c}$ adsorption position, $\Delta E_{\text{ads}}$ is positive and the process is spontaneous. For each kind of adsorption models, the adsorption energy of H$_2$ on O$_{2c}$ is relatively higher than others, demonstrating that it is the optimal site in the slab model and the probability of adsorption is the largest. This result is consistent with that reported in [37].

Compared with pure SnO$_2$, the adsorption energy of Cu-doped SnO$_2$ is greatly increased. The doping of Cu would facilitate the adsorption of H$_2$. In particular, the adsorption energy on Cu$_{5c}$ is positive, and it means that the H$_2$ molecular prefers adhesive to the atom. Moreover, Cu becomes an additional adsorption site in the lattice and its presence would further enhance the sensitivity to H$_2$. It should be pointed out that it is unlikely to determine the exact adsorption energy due to the deviations between the experimental condition and the theoretical model. However, the trend is reliable [31].

Table 4: Adsorption energy of H$_2$ adsorbed on Cu-doped and pure SnO$_2$ surface (unit, eV).

<table>
<thead>
<tr>
<th>Adsorption energy</th>
<th>O$_{3c}$</th>
<th>O$_{5c}$</th>
<th>Sn$_{5c}$</th>
<th>Sn$_{6c}$</th>
<th>Cu$_{5c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure-SnO$_2$</td>
<td>0.054</td>
<td>-0.041</td>
<td>-0.017</td>
<td>0.073</td>
<td>—</td>
</tr>
<tr>
<td>Cu-SnO$_2$</td>
<td>0.367</td>
<td>-0.337</td>
<td>-0.299</td>
<td>0.351</td>
<td>0.286</td>
</tr>
</tbody>
</table>

3.2.2. Electronic Structure. To gain an insight into the interaction between H$_2$ and SnO$_2$ surface, the electronic structure of SnO$_2$ surface is analysed. Since O$_{2c}$, Sn$_{5c}$, and Cu$_{5c}$ are energetically favourable position for H$_2$ adsorption, this study mainly focuses on these sites. Figure 5 shows the TDOS of SnO$_2$ surface. It can be found that the profile, the magnitude, and the width have no obvious change after the adsorption. The adsorption does not inject any electronic state into the band gap of the surface, which is similar to CO adsorption on Pd-doped SnO$_2$ surface [26].

Figures 6, 7, and 8 show the PDOS of free H$_2$, H$_2$ adsorbed on pure surface and H$_2$ adsorbed on Cu-doped surface, respectively. The PDOS of O$_{2c}$, Sn$_{5c}$, and Cu$_{5c}$ near Fermi level, ranging from ~6 eV to 6 eV, are also included.
In contrast, there are prominent changes for the DOS of \( \text{H}_2 \) after adsorption, and the DOS of free \( \text{H}_2 \) (see the dash line) is located near the Fermi level. While adsorbed on the SnO\(_2\) surface, the DOS of \( \text{H}_2 \) had a shift towards the lower energy side. Compared with the adsorption on the pure SnO\(_2\) surface, the DOS of \( \text{H}_2 \) adsorbed on Cu-doped SnO\(_2\) surface is closer to the Fermi level, indicating a greater activity and the facilitation of orbital hybridizations between orbits.

Amongst the adsorption models, the DOS of \( \text{H}_2 \) adsorbed on O\(_{2c}\) (both pure and Cu-doped SnO\(_2\) surface) and Cu\(_{5c}\) (Cu-doped SnO\(_2\) surface) are split into two peaks, which implies that the interaction between the molecular of \( \text{H}_2 \) and the surface is quite strong in the adsorption process.

From Figures 6 to 8, it can be also found that the DOS of \( \text{H}_2 \) is broadened, which facilitates the formation of chemical bonds through orbital hybridization. \( \text{H}_2 \) adsorption on the surface is mainly due to the interaction between the s orbital states of \( \text{H}_2 \) molecules and the p orbital states of O, s and p orbital states of Sn, and d orbital states of Cu atom. A larger amount of electrons would be transferred in the gas sensing process. Cu doping would enhance the sensitivity to \( \text{H}_2 \), and the theoretical analysis presented in Section 3.1.2 is further confirmed.

3.2.3. Mulliken Population Analysis. Space charge analysis provides an approach to estimate the partial atomic charges and the electrical conductance. The most commonly used methods are Mulliken and Bader’s charge analysis [29]. However, Bader charges sometimes yield too extreme values that suggest much ionic character even in the case of covalent bonds. Mulliken population analysis [17, 26, 27, 37, 38] is employed herein to study the charge transfer between SnO\(_2\) surface and \( \text{H}_2 \). \( \text{H}_2 \) adsorption on five potential coordinated sites is considered, as listed in Table 5.

The charges of free \( \text{H}_2 \) are obtained by summing the charges of two individual atoms. It is clearly that the bond length of \( \text{H}_2 \) varies significantly after adsorption, from 0.74 Å of free \( \text{H}_2 \) to 0.84 Å, 0.86 Å, 0.77 Å, 1.66 Å, and 0.70 Å when adsorbed on O\(_{2c}\), O\(_{3c}\), Sn\(_{5c}\), Sn\(_{6c}\), and Cu\(_{5c}\), respectively. It indicates that \( \text{H}_2 \) adsorption tends to disassociate. Such
results are similar to H$_2$ adsorption on pure SnO$_2$ surface [38] and H$_2$S adsorption on Cu-doped SnO$_2$ surface [34].

When H$_2$ is adsorbed on pure SnO$_2$ surface, the gas molecule would withdraw charges from the surface. Similar behaviours have also been obtained by Bechthold et al. [18], Menetrey et al. [39], and Sun et al. [40]. Using the first principle method based on DFT, it has been found that the clean SnO$_2$ surface transfers charges to CO molecule, making it negatively charged.

Regarding Cu-doped SnO$_2$ surface system, charges are conveyed mainly from H$_2$ molecular to the surface. The amount of electrons lost by H$_2$ is as high as 0.79 e, which is much higher than that of pure SnO$_2$ system. The electrons would be received by the surface and then injected back into the conduction band. Thus, the carrier density of the conduction band would be increased. In addition, both the barrier height of surface depletion layer and the resistance of SnO$_2$ would decline, leading to the acceleration of the current flowing through the surface and the increment of the output signal of the associated sensors. Consequently, the sensitivity of the sensor towards H$_2$ would be significantly enhanced. In summary, the doping of Cu would improve the adsorption performance of SnO$_2$-based sensor toward H$_2$.

### 4. Conclusions

In this work, the adsorption mechanism of Cu-doped SnO$_2$ surface toward H$_2$ has been studied. The main conclusions are drawn as follows.

(i) The O$_{2c}$ atom is the most favourable adsorption position for hydrogen on both pure and Cu-doped surfaces. The Cu atom provides an additional adsorption site in the lattice after doping, and its presence can contribute to the gas sensing process.

(ii) Since the d states electrons of Cu are injected into the band gap and the conduction band is moved to lower energy area, the band gap of SnO$_2$ surface is narrowed. The doping of Cu facilitates the migration of carriers between the valence band and the conduction band.

(iii) The PDOS of H$_2$ after adsorption is broadened and shifted closer to the Fermi level. The interaction between H$_2$ and the surface is mainly due to the orbital hybridization between the s states of H$_2$ molecules and the p states of O, s and p states of Sn, and d states of Cu atom.

(iv) After Cu doping, the quantity of electrons transferred from H$_2$ molecular to SnO$_2$ surface is substantially increased. The electrons would be captured by the surface and then released back into its conduction band, leading to the reduction of resistance and the enhancement of sensitivity toward H$_2$.

### Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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