Cu₄ Cluster Doped Monolayer MoS₂ for CO Oxidation

Z. W. Chen, J. M. Yan, W. T. Zheng & Q. Jiang

The catalytic oxidation of CO molecule on a thermodynamically stable Cu₄ cluster doped MoS₂ monolayer is investigated by density functional theory (DFT) where the reaction proceeds in a new formation order of COOOCO* (O₂* + 2CO* → COOOCO*), OCO* (COOOCO* → CO₂ + OCO*), and CO₂ (OCO* → CO₂) desorption with the corresponding reaction barrier values of 0.220 eV, 0.370 eV and 0.119 eV, respectively. Therein, the rate-determining step is the second one. This low barrier indicates high activity of this system where CO oxidation could be realized at room temperature (even lower). As a result, the Cu₄ doped MoS₂ could be a candidate for CO oxidation with lower cost and higher activity without poisoning and corrosion problems.

With the rapid development of industry, the amount of carbon monoxide (CO) emission, resulted from automobiles, industrial processes and so on, drastically increases. Currently, the most effective way in reducing CO is CO oxidation where the decrease of the energy barrier values (Eₐ) with effective catalysts is most technically concerned. Besides the element metals, such as Pt, Pd, Ru, Au, etc., alloys, oxides and others are also selected as catalysts, where the higher activity, the higher oxidation and poison resistances, and the lower cost, are important indexes.

Single atomic metal catalyst anchored on appropriate support has the maximal usage of metal atoms and great potential to achieve high activity and selectivity. The difficulty of this usage is its aggregation into big clusters on the support due to the high surface free energy of metal atoms. Supported metal clusters are an alternative choice. For instance, MgO supported Au₈ cluster and Fe₃O₄ supported Pdₙ clusters show good catalytic activities for CO oxidation where the catalytic activities of supported metal clusters are strongly size-dependent and shape-dependent.

Copper-based catalysts or catalyst promoters have attracted persistent interests because of their wide applications in a variety of industrial processes. For instance, copper-based nanoparticles supported on oxide substrates show superior catalysis for low temperature CO oxidation and resistance against water contamination. The Cu embedded in graphene has been proved to be a good candidate for CO oxidation with lower cost and higher activity. However, easy oxidation of Cu atoms leads to low service life of copper-based catalysts.

Graphene is a promising matrix supporting metal atoms to catalyze CO oxidation due to its outstanding electrical, mechanical and thermal properties with large surface/volume ratio. However, the thermal stability and chemical reactivity issues associated with graphene may hinder its applications due to weaker anchoring ability of atoms and clusters and less controlling ability of the shapes of atoms and clusters resulted from graphene's single-layer structure. The monolayer MoS₂ has a similar two-dimensional (2D) structure of graphene and is inert due to the absence of dangling bonds at the basal planes terminated by S atoms. Differing from graphene, MoS₂ monolayer consisting of S-Mo-S sandwich layer could well fix and regulate the morphology of clusters as expected. It could be an alternative of graphene and has been acted as the catalyst for the hydrogen evolution reaction (HER) and CO oxidation.

In this work, the tetrahedral structure of four Cu atoms (Cu₄) embedded in monolayer MoS₂ is carried out through first principles calculations where one Mo atom and three S atoms in the monolayer MoS₂ are substituted by Cu₄ since the unique triangular active site of Cu₄ has been identified as a crucial role.
for CO oxidation. This structure is stable due to the strong chemical bonds among Cu$_4$ and monolayer MoS$_2$ while the triangular Cu$_3$ active site is acted for CO oxidation by adsorbing O$_2$ and more CO molecules and the Cu$_4$ cluster completely inserts into the sandwich of MoS$_2$. We have found a new OCO* intermediate state (MS) with a small $E_{\text{bar}}$ of 0.370 eV on Cu$_4$ cluster during the CO oxidation process. Our calculations suggest that the Cu$_4$ cluster embedded in a monolayer MoS$_2$ is a good candidate for CO oxidation.

**Results and discussion**

The experimental fabrication of the Cu$_4$ doped MoS$_2$ could be intricate since there are two different doping sites on monolayer MoS$_2$, Mo vacancy and S vacancy. It is known that Re atoms and Co atoms occupying Mo sites in monolayer MoS$_2$ have been synthesized by the chemical vapor transport (CVT) and chemical vapor deposition (CVD) method, respectively. Since the value of Pauling electronegativity of Cu (1.90) is almost the same of Re (1.90) and Co (1.88), the Cu atom could substitute Mo atom in the MoS$_2$ by means of CVT or CVD, which has been proved to be feasible through the density functional calculations. Then, the S vacancies are prepared by low-energy argon sputtering or electron irradiation. Last, the Cu$_3$ atoms are embedded into these vacant sites through the physical vapor deposition. The corresponding structure of Cu$_4$ doped MoS$_2$ is shown in Fig. 1(a) where one Cu atom substituting the Mo atom is denoted as Cu$_1$, and the other three Cu atoms replacing three S atoms on the surface of monolayer MoS$_2$ are named as Cu$_3$. The flat triangular Cu$_3$ active site on the surface plays a vital role for CO oxidation. The Cu$_3$ atoms and surface S atoms are at the same plane, making it less active to be oxidized than the metal atoms above the graphene surface. The bond lengths of Cu$_3$-Cu$_3$ and Cu$_3$-Cu$_1$ are 2.53 Å and 2.57 Å, being almost the same of Cu-Cu (2.55 Å) in Cu bulk. The bond lengths of Cu$_3$-Mo and Cu$_1$-S are 2.66 Å and 2.28 Å. The latter is shorter than the bond length of Cu-S of 2.41 Å in Cu-doped MoS$_2$. Thus, Cu$_1$-S bond is stronger than Cu-S bond. From Hirshfeld charge analysis, the electron transfer of Cu$_1$ and Cu$_3$ are 0.146 e and 0.076 e, respectively. The direction of electron transfer is in agreement with the values of Pauling electronegativity of Cu (1.90), S (2.58) and Mo (2.16). There are about 0.374 e transfer from the Cu$_1$ cluster to monolayer MoS$_2$. The electron transfer can also be verified by the charge density difference (CDD) for Cu$_4$ doped MoS$_2$. As shown in Fig. 1(b), the blue and red regions represent the areas of electron accumulation and depletion, respectively. Obviously, different electron affinities of Cu, S and Mo determine the electron distribution. The pronounced charge density...
redistribution on the Cu₃-Mo bonds and Cu₁-S bonds [Fig. 1(b)] indicates stronger interaction between Cu₄ and MoS₂.

The partial density of states (PDOS) projected on the 3d orbitals of Cu₁, the 2p orbitals of its neighboring S, 3d orbitals and 4s orbitals of Cu₃ and 4d orbitals of its neighboring Mo are plotted, as shown in Fig. 1(c),(d). The strong interaction between Cu₁ and S can be further confirmed by the PDOS in Fig. 1(c) where significant hybridization between Cu₁-3d and the adjacent S-2p is present, denoting the stability of the system. Furthermore, the hybridization between 4s and 3d orbitals of Cu₃ and the adjacent Mo-4d is also found in Fig. 1(d).

To gain more insight into the stability of Cu₄ doped MoS₂, we also calculated the E_b of Cu₄ doped MoS₂, being 3.262 eV, showing strong interaction between Cu₄ cluster and its neighboring S and Mo atoms. For the possible diffusion problem of Cu atom, we computed the energy barrier and reaction energy of Cu diffusion. Since the Cu₄ strongly bonds with three S atoms and it is in the middle layer of the Cu₄ doped MoS₂, the diffusion of the Cu₁ atom is difficult. Therefore, only the surface Cu₃ atoms are considered here. Because all three Cu₃ atoms are the same in symmetry, we study only one Cu₃ atom diffusing to the neighboring hollow site or Mo top site [Fig. 2(a)]. The diffusion energy barriers for the two cases are the same with a value of 1.41 eV and the reaction energies are 1.02 eV and 1.22 eV, respectively. Considering the high diffusion barriers and the endothermic reactions, the diffusion of Cu₃ is absent and the Cu₄ doped MoS₂ system thus is an energetically stable structure.

To further prove the stability of the system, first principle molecular dynamics (MD) simulation at a constant temperature of T = 500 K in the NVT ensemble (i.e., constant particle number, volume and temperature condition) has been carried out for 5 ps with the time step of 1 fs. Three structures from MD calculation are present in Fig. 2(b). It is found that Cu₄ cluster is fixed in the vacancies of MoS₂ and the Cu atoms are located at the original sites after 5000 dynamics steps at 500 K. Thus, the stability of the studied Cu₄ doped MoS₂ system at room temperature is expected.

The adsorption process of O₂ molecule on Cu₄ doped MoS₂ is considered for possible side-on and end-on configurations. With the former configuration, two found adsorption structures of O₂ molecule are shown in Fig. 3(b),(c), which are defined as t-h-b and b-h-b with E_ad-O₂ values of −1.743 eV and

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Figure 2. (a) The diffusion paths of the Cu atom from the S vacancy to its neighboring hollow site of the S-Mo-S hexagonal ring (left) and Mo top site (right), including the initial state (IS), transition state (TS), and final state (FS). The values (in eV) show all energies are given with respect to the reference energy. (b) The three structures from MD simulation in 5 ps at the temperature of 500 K are shown.
With the latter configuration, there are three adsorption structures. The related $E_{\text{ad}}$ values are $-0.867 \text{ eV}$, $-0.868 \text{ eV}$ and $-0.602 \text{ eV}$ on hollow, bridge and top sites. The above results imply that the $O_2$ molecule prefers the side-on configurations, which gets $0.399 \text{ eV}$ and $0.420 \text{ eV}$ respectively.

**Table 1.** The adsorption energies $E_{\text{ad},M}$ of the $O_2$ or CO, $E_{\text{ad},nCO}$ values of $4 \times 4$ and $3 \times 3$ supercell of the Cu$_4$ doped monolayer MoS$_2$. The negative sign means exothermic process. The values in parentheses represent $E_{\text{ad}}$ values of another configuration.

| Supercell | $4 \times 4$ | $3 \times 3$ |
|-----------|--------------|--------------|
| $E_{\text{ad},CO}$ | $-1.105 \text{ eV}$ | $-1.095 \text{ eV}$ |
| $E_{\text{ad},O_2}$ | $-1.743 \text{ eV} \text{ (}-1.749 \text{ eV}\text{)}$ | $-1.731 \text{ eV} \text{ (}-1.741 \text{ eV}\text{)}$ |
| $E_{\text{ad},1CO}$ | $-0.401 \text{ eV}$ | $-0.420 \text{ eV}$ |
| $E_{\text{ad},2CO}$ | $-0.350 \text{ eV} \text{ (}-0.315 \text{ eV}\text{)}$ | $-0.351 \text{ eV} \text{ (}-0.351 \text{ eV}\text{)}$ |
| $E_{\text{ad},3CO}$ | $-0.186 \text{ eV}$ | $-0.235 \text{ eV}$ |

$-1.749 \text{ eV}$ (Table 1). With the latter configuration, there are three adsorption structures. The related $E_{\text{ad},O_2}$ values are $-0.867 \text{ eV}$, $-0.868 \text{ eV}$ and $-0.602 \text{ eV}$ on hollow, bridge and top sites. The above results imply that the $O_2$ molecule prefers the side-on configurations, which gets $0.399 \text{ eV}$ and $0.420 \text{ eV}$ respectively.
Being consistent with the Hirshfeld charge analysis, the PDOS of O₂ molecule, adsorbed O₂ and Cu atom are shown in Fig. 4(c),(d). All orbitals of O₂ are labeled while the 2π* anti-bond orbital is half filled, which is in agreement with literature data 45. When O₂ is adsorbed on Cu₁, significant charge transfers (0.420 e and 0.399 e) from Cu₄ doped MoS₂ to O₂ are found, which occupy the initial empty component of the O₂-2π* orbitals and lead to the elongation of the O-O bond from 1.224 Å to 1.484 Å and 1.467 Å respectively. The hybridization between Cu atom and O₂-2π* orbitals is located near Fermi level.

For CO oxidation reaction, the adsorption of CO and CO₂ also should be considered. In this system, the E_ad-CO values are −1.105 eV on top site, −0.990 eV on bridge site and −0.957 eV on hollow site, respectively. Thus, CO prefers adsorbing on the top site, as illustrated in Fig. 3(a). Since E_ad-O₂ (−1.749 eV) is stronger than E_ad-CO (−1.105 eV), O₂ is preferentially adsorbed on the hollow site, which indicates there is no CO poisoning problem. And the E_ad-CO₂ value is −0.140 eV, which proves that the CO₂ is easy to leave the surface. Note that as long as the first O₂ is adsorbed on the hollow site, sites for other O₂ adsorptions are absent. Because the adsorption energy value of two O₂ on the catalyst is −1.709 eV, which is weaker than that of only one O₂. As a result, the Cu₄ doped MoS₂ without poisoning and oxidation problems could be a good catalyst with a long cycle life. To further more comprehensively understand the adsorption of O₂ and CO on the catalyst, the other sites near the Cu₄ cluster are considered. Because MoS₂ surface is inert at the basal planes terminated by S atoms, both E_ad-O₂ value and E_ad-CO value are about −0.1 eV, which imply that O₂ and CO only are adsorbed on Cu₄ cluster of the catalyst.

All configurations and their E_ad-nCO values are given in Table 1. For the co-adsorption of O₂ + nCO, the E_ad-nCO are −0.401 eV, −0.350 eV and −0.186 eV respectively for n = 1, 2, 3. The corresponding PDOS of Cuⁿ and Cuⁿ-CO are shown in Fig. 5. When n = 1 and 2, the orbitals below Femi level are away from the Femi level, denoting more stable states. If n = 3, however, the orbitals change less, denoting weaker interaction of the third CO with Cu atom. To simplify the latter discussion, we neglect the adsorption of the third CO on Cu₄ cluster in the following.

Now we begin to consider CO oxidation on Cu₄ doped MoS₂. It is well known that there are two mechanisms for CO oxidation: Langmuir-Hinshelwood (LH) mechanism and Eley-Rideal (ER) mechanism. The former involves all the reacting intermediates on the surface, whereas the latter does species from the direct reaction with a surface intermediate 46,47. Both will be discussed in details in the following.

Firstly, the LH mechanism of the one CO co-adsorption with O₂ molecule is considered, which is denoted as mLH shown in Fig. 6 (top views in Fig. S1). The O atom in O₂ molecule approaches the surface. The O-O bond breaks and CO₂ molecule is released from the surface with a energy intermediate state (MS1 in Fig. 6) with the E_sur = 0.302 eV. Then, the O-O bond breaks and CO₂ molecule is released from the
catalyst with $E_{\text{bar}} = 0.292$ eV. Therein, the rate-determining step for the mLH mechanism is the formation of OCOO* intermediate (TS1 in Fig. 6). On the other hand, for mER mechanism, the first un-adsorbed CO molecule directly reacts with the activated O$_2$ molecule. Due to the presence of two adsorption configurations of O$_2$ molecule, there are two kinds of mER mechanisms in the reaction path (mER in Fig. 6). The migration of CO molecule toward the pre-adsorbed O$_2$ molecule is determined as the rate-determining step with $E_{\text{bar}} = 0.385$ eV (TS3 and TS4 in Fig. 6). When the O$_2$ molecule and first CO molecule have been adsorbed on the triangular Cu$_3$ active site, the second CO molecule can be further adsorbed, which reacts with the adsorbed O$_2$. We assume that the reaction could follow bLH mechanism or bER mechanism, we define b denoting the case where two CO molecules are involved in the reaction path. In the bLH mechanism, the adsorption structures of the two CO molecules and O$_2$ molecule are shown in Fig. 3(e),(f). The initial structure of Fig. 3(f) goes to the OC-OCOO* intermediate state (MS2 in Fig. 6) with $E_{\text{bar}} = 0.220$ eV (while another [Fig. 3(e)] does not), where the O-O bond is broken up and two metastable states are present (FS4 and FS5 in Fig. 6). Their $E_{\text{bar}}$ values are 0.364 eV and 0.370 eV, respectively. Although both values are pretty much the same, the product of FS5, OCO*, releases 0.22 eV more energy for the formation of first CO$_2$ than that of FS4 while OCO* is beneficial for the next oxidation reaction. As a result, FS5 tends to happen relative to FS4. In the case of bER mechanism (Fig. 6), $E_{\text{bar}} = 0.381$ eV for the release of the first CO$_2$.

After releasing the first CO$_2$, the following structures are shown in Fig. 6(FS1~FS6). In addition to OCO* (FS5), others have one O atom on the triangular Cu$_3$ site. The O atom needs larger $E_{\text{bar}}$ to form CO$_2$ with CO due to the strong interaction between the Cu$_3$ atoms and O atom, as shown in Fig. S2. However, the formation of CO$_2$ from the OCO* intermediate state has the smallest $E_{\text{bar}}$ (0.119 eV) to escape from the surface of the catalyst, implying desorption of the second CO$_2$. The above results show that the LH mechanism is better than the corresponding ER mechanism as the O$_2$ molecule itself is not activated enough without the cooperative adsorption of CO. Then, the co-adsorbed CO molecules affect the $E_{\text{bar}}$ while the rate-determining step changes from the first step to the second one. The $E_{\text{bar}}$ of ER mechanism is affected by the adsorbed number of CO molecule too. Last, it should be noted that in the bLH mechanism, the OCO* (FS5 in Fig. 6) is found as the last product which is particularly favorable for the release of the second CO$_2$ with $E_{\text{bar}} = 0.119$ eV. As a result, the most optimal reaction path is given in Fig. 7. Among three $E_{\text{bar}}$ values in the reaction path, the largest $E_{\text{bar}}$ value is 0.370 eV where the rate-determining step is the formation of the OCO* intermediate state. Thus, no matter from the point of view of dynamics or thermodynamics, the reaction path (Fig. 7) is the most optimal process. Because of the complexity and diversity of the experimental conditions, there are a few other reaction paths in CO oxidation reaction. All kinds of reaction paths and their $E_{\text{bar}}$ values are shown in Fig. S3 and Fig. S4.

Now we compare the corresponding $E_{\text{bar}}$ values at the rate-determining reaction step for our system and related systems which are listed in Table 2. As shown in Table 2, Zn-embedded graphene and Au-embedded graphene have smaller $E_{\text{bar}}$ than this system. However, it is noteworthy that our system is more stable than Zn-embedded graphene while Au-embedded graphene has CO poisoning problem, thus their applications are limited. Thus, the overall performance of Cu$_4$ doped MoS$_2$ for the CO oxidation should be the best among the considered systems.

Under the biggest doping concentration, Cu$_4$ doped 3 × 3 monolayer MoS$_2$ supercell is also considered for CO oxidation. For CO and O$_2$ adsorption, their adsorption energy values are shown in Table 1 where the both supercells have almost the same values. The stability of 3 × 3 supercell is also determined,
As shown in Fig. S5, the results show that even Cu4 doped monolayer MoS2 has the biggest doping concentration, it still possesses good catalytic activity and stability for CO oxidation as our results from the 4 × 4 supercell studied above.

In summary, our comprehensive DFT studies of CO oxidation on Cu4 doped monolayer MoS2 suggest that the protruded triangular Cu3 site is the main active site for CO catalytic oxidation while the number of CO adsorbed molecule produces a significant effect on the energy barriers of the CO oxidation reaction. During the reaction, an OCO* intermediate state is found, which leads to the energy barrier of CO oxidation of 0.370 eV. As a result, the Cu4 doped monolayer MoS2 with outstanding catalytic activity without poisoning and oxidation problems could be a good candidate for CO oxidation with low cost and high activity.

**Methods**

In this work, all calculations are performed using the spin-unrestricted density functional theory (DFT) as implemented in the DMol3 code48. Exchange-correlation functions are taken as a generalized gradient approximation (GGA) with Perdew-Wang correlation (PWC)49. DFT semi-core pseudo potentials (DSPPs) core treatment50 is implemented for relativistic effects, which replaces core electrons by a single effective potential. In addition, double numerical plus polarization (DNP) is chosen as the basis set and the quality of orbital cutoff is fine. The convergence criteria of the geometrical optimization are set.

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**Figure 6.** The reaction paths (side views) of the mLH, mER, bLH and bER of the first CO2 release. m: monomolecular (only one CO molecule); b: bimolecular (two CO molecules); IS: initial state; MS: intermediate state; TS: transition state; FS: final state. The values are the relative energies and in unit of eV.
to be $1.0 \times 10^{-5}$ hartree for the energy change, $2.0 \times 10^{-3}$ hartree/Å for the gradient, and $5.0 \times 10^{-3}$ Å for the displacement, respectively. The smearing parameter is set to be 0.005 hartree in the geometric optimization. For transition states (TS) searching, the calculation firstly performs a linear synchronous transit (LST) maximum, which is followed by an energy minimization in directions conjugating to the reaction pathway. TS approximation obtained via LST/optimization is then used to perform a quadratic synchronous transit (QST) maximization to find more accurate transitional states. The convergence tolerance of the root mean square (RMS) force is $2.0 \times 10^{-3}$ hartree/Å and the maximum number for QST step is set as 10. In the simulation, three-dimensional periodic boundary conditions are taken. The simulation cell consists of a $4 \times 4$ monolayer MoS$_2$ supercell with a vacuum width of 18 Å, which leads to negligible interactions between the system and their mirror images. In order to prove the effect of doping concentration, $3 \times 3$ monolayer MoS$_2$ supercell is also considered. For geometric optimization and the search for the transition state (TS), the Brillouin zone integration is performed with $3 \times 3 \times 1$ k-point sampling. After structure relaxations, the density of states (DOS) are calculated with a finer k-point grid.

Figure 7. The most optimal reaction path of CO catalytic oxidation.

Table 2. The $E_{\text{bar}}$ values of rate-determining reaction of different systems.

| Systems                          | $E_{\text{bar}}$ (eV) | Reference   |
|---------------------------------|-----------------------|-------------|
| Cu$_4$-doped monolayer MoS$_2$  | 0.37                  | This work   |
| Cu-doped graphene               | 0.59                  | 26          |
| Fe-doped monolayer MoS$_2$      | 0.51                  | 38          |
| Au-doped h-BN monolayer         | 0.47                  | 32          |
| graphene/Pt (1 1 1)             | 0.51                  | 5           |
| Zn-embedded graphene            | 0.26                  | 29          |
| Au-embedded graphene            | 0.31                  | 30          |
of $15 \times 15 \times 1$ to achieve high accuracy, and the empty bands are chosen as 12. Concerning with the properties of charge transfers, atom charges would be calculated via the Hirshfeld population analysis\(^{22,33}\).

In the above system, the binding energy value $E_b$ (Cu\(_4\)) is defined as\(^{34}\),

$$E_b(Cu_4) = \frac{[E(Cu_4/MoS_2) - 4E(Cu) - E(MoS_2)]}{4} \quad (1)$$

where $E(MoS_2)$, $E(Cu)$ and $E(Cu_4/MoS_2)$ are the total energies of the monolayer MoS\(_2\) with three S vacancies and a Mo vacancy, the free Cu atom, and the Cu\(_4\) doped MoS\(_2\), respectively.

For one molecule (CO, O\(_2\), CO\(_2\)) adsorbed on catalyst, the adsorption energy values of $E_{ad-M}$ (the subscript M denotes the corresponding molecule) are determined by,

$$E_{ad-M} = E_{mol/cat} - (E_{cat} + E_{mol}) \quad (2)$$

where $E_{mol/cat}$, $E_{cat}$ and $E_{mol}$ are total energies of the molecules/catalytic system, the isolate catalyst, and the molecule.

For several molecules (CO and O\(_2\)) co-adsorbed on the catalyst, the adsorption energy value $E_{ad-nCO}$ is determined by,

$$E_{n} = E_{mol/cat} - (E_{cat} + E_{O_2} + nE_{CO}) \quad (3)$$

where $E_{O_2}$ and $E_{CO}$ are total energy values of O\(_2\) and CO, and $n$ represents the number of CO.

The van der Waals interaction is taken into account by using DFT-D functional in Dmol\(^3\). The $E_{ad-CO}$ and $E_{ad-O_2}$ values recalculated are now $-1.226$ eV and $-1.842$ eV respectively, which are a little stronger than the values of $E_{ad-CO} = -1.105$ eV and $E_{ad-O_2} = -1.749$ eV calculated without the consideration of the van der Waals interaction. About the reaction processes, we study the most optimal path and the rate-determining steps of all reaction paths. The reaction barrier values of $O_2^* + 2CO^* \rightarrow$ COOOOCO*, COOOOCO* $\rightarrow CO_2 + OC^* + OCO^*$ and $O_2 + COO^* \rightarrow CO_2$ for the path of CO oxidation remains correct.

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Supplementary information
Additional Information

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Q.J. conceived and designed the material. Z.W.C. carried out the simulation. Z.W.C. and Q.J. wrote the manuscript. J.M.Y. and W.T.Z. entered the discussion. All authors commented on the manuscript.

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