Achieving high-temperature ferromagnetism by means of magnetic ions dimerization

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Magnetic two-dimensional materials have potential application in next-generation electronic devices and have stimulated extensive interest in condensed matter physics and material fields. However, how to realize high-temperature ferromagnetism in two-dimensional materials remains a great challenge in physics. Herein, we propose an effective approach that the dimerization of magnetic ions in two-dimensional materials can enhance the exchange coupling and stabilize the ferromagnetism. Manganese carbonitride Mn2N6C6 with a planar monolayer structure is taken as an example to clarify the method, in which two Mn atoms are gathered together to form a ferromagnetic dimer of Mn atoms and further these dimers are coupled together to form the overall ferromagnetism of the two-dimensional material. In Mn2N6C6 monolayer, the high-temperature ferromagnetism with the Curie temperature of 272.3 K is determined by solving Heisenberg model using Monte Carlo simulations method.

INTRODUCTION

Owing to the reduced dimensionality and symmetry, two-dimensional (2D) materials possess a variety of unique qualities associated with exotic and fantastic physical phenomena, which provide tremendous opportunities in both fundamental study and potential application research. Since graphene was discovered in 2004 [1], 2D materials have attracted great attention from researchers in physics and material fields. In experiments, various 2D materials have been fabricated, such as boron nitride [2], silicene [3], borophene [4], stanene [5], transition metal dichalcogenides [6], MXenes [7], etc. Meanwhile, theoretical researches have designed and predicted a variety of 2D compounds, such as Si2BN [8], B3C2 [9], Fe2Si [10], CoB6 [11], and so on. However, among the reported 2D materials, the proportion of magnetic 2D compounds is very small.

Ferromagnetic 2D material is a kind of highly promising material for the next-generation spintronic devices including giant magneto-resistance, spin valve, magnetic random-access memory and other spin logic devices, and the research on 2D ferromagnet is extremely vigorous in recent years. In 2017, long-range ferromagnetic ordering was first discovered in CrI3 monolayer by scanning magneto-optic Kerr microscopy and the Curie temperature is 45 kelvin.[12] Subsequently, ferromagnetic order in exfoliated Cr2Ge2Te6 bilayer was observed,[13] and the Curie temperature of 330 kelvin in VS2 monolayer was also reported.[14] Very recently, robust room-temperature ferromagnetism with TC up to 400 K has been realized in CoN4-embedded graphene.[15] In theoretical studies, CrI3 [16], CrGeTe3 [17], Fe2Si [10], MnS2 [18], Fe3P [19], CrMoS2Br2 [20], GaI2 [21], CrN4C2 [22] monolayers are predicted to be 2D ferromagnet with high Curie temperature.

Although some progress has been made, the study on ferromagnetic 2D materials is still in the primary stage. Curie temperature is a decisive physical parameter to the properties of ferromagnetic materials. At present, Curie temperature much lower than room temperature is the main obstacle to the applications of 2D ferromagnets in magnetic device fabrication. A natural and fundamental question is how to enhance the Curie temperature of a 2D ferromagnet. Multiple factors can influence the Curie temperature of 2D materials. Specifically, it depends on the exchange coupling between magnetic ions, the spin of each ion, and magnetic anisotropic energy, and the type of crystal lattice. A few schemes including strain, carrier doping, adsorption, and proximity effect are employed to enhance the exchange interaction in the known 2D materials. [23, 24] In these methods, the spin S only refers to single atom spin and the coupling J is only related two single atoms, rather than the clusters of magnetic atoms, which gives rise to small S and J and limits the realization of high critical temperature.

In this work, we propose a radically different strategy to enhance magnetic exchange energy. First, two magnetic ions are gathered together to form a ferromagnetic dimer as one lattice point, which has a larger total spin and magnetic anisotropic energy than single magnetic ion. Then, a suitable distance between two dimers is chosen to ensure a strong magnetic exchange coupling. In previous experiments, the dimers of transition metal atoms were embedded in N-doped graphene to synthesize the dual-atom catalyst [25], and even the structural unit of Mn trimer was also realized in recently synthesized MnSn multilayer[26]. These clusters of two or three atoms are embedded in the two-dimensional monolayer and are small enough to be regarded as a lattice point on a two-dimensional lattice. Based on the above idea and the experimental works, we screen out the planar Mn2N6...
as a basic unit, which is a Mn dimer and has total magnetic moments up to 7.3 $\mu_B$. Then, the Mn$_2$N$_6$ moieties are embedded in graphene lattice to make up a hybridized monolayer with the distances among Mn$_2$N$_6$ moieties as short as possible. After much trial and error, we design a 2D manganese carbonitride Mn$_2$N$_6$C$_6$ with the Curie temperature of 272 K, which is a fairly near-room-temperature predicted by the Heisenberg model [23].

**COMPUTATIONAL METHOD**

The calculations are performed in VASP package, in which the plane wave pseudopotential method and the projector augmented-wave (PAW) pseudopotential with Perdew-Burke-Ernzerhof (PBE) functional [27-30] are adopted, and Hubbard U is included to consider the correction of electron correlation within GGA + U method [31]. The plane wave basis cutoff is 600 eV and the thresholds are $10^{-5}$ eV and 0.01 eV/Å for total energy and force convergence. The interlayer distance was set as 18 Å and a mesh of $24 \times 24 \times 1$ k-points is used for the Brillouin zone integration. The phonon calculations are carried out with the supercell method in the PHONOPY program, and the real-space force constants of supercells were calculated using density-functional perturbation theory (DFPT) as implemented in VASP [32]. The force convergence criterion ($10^{-5}$ eV/Å) was used in structural optimization of the primitive cell before building the supercell. In the ab initio molecular dynamics simulations, the $2 \times 2 \times 1$ supercells were employed and the temperature was kept at 1000 K for 5 ps with a time step of 1 fs in the canonical ensemble (NVT) [33].

The temperature of phase transition in Mn$_2$N$_6$C$_6$ systems is evaluated by solving the Heisenberg model with Monte Carlo method, implemented in the Mcsolver package [34, 35]. Monte Carlo simulations are performed with a $60 \times 60 \times 1$ spin lattice in which the spins interact with each other. For one temperature value, the system of spins corresponds to one thermal equilibrium state, and the related statistics observables such as energy and magnetic moment are directly obtained and other physical quantities can be derived. The average moment and the specific heat capacity are expressed as $M = \frac{1}{N} \sum_i |\vec{M}_i|$ and $C_v = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}$.

**RESULTS AND DISCUSSION**

Fig. 1(a) shows the crystal structure of Mn$_2$N$_6$C$_6$ monolayer, which consists of six-members carbon rings and Mn$_2$N$_6$ moieties, depicted with the dashed line rectangle. The two components are arranged alternately to form a planar layer, in which all nitrogen and carbon atoms are tricoordinated and metal atoms are tetracoordinated. The primitive cell of Mn$_2$N$_6$C$_6$ is displayed with a solid line rhombus and has the symmetry of plane group C$mmm$, shown in Fig. 1(b). In Mn$_2$N$_6$ moiety, two MnN$_4$ units are fused together by two shared N atoms, which results in the dimerization of two adjacent Mn atoms. Fig. 1(c) shows the charge density difference relative to atomic charge density, in which yellow and blue surfaces depict the charge accumulation and depletion. Yellow surfaces between N and Mn atoms indicate the formation of N-Mn coordination bonds, while three yellow pockets around N and C atoms reflect their $sp^2$ orbital hybridization and the N-N and N-C covalent bonds. So the framework made up of C and N atoms with $sp^2$ orbital hybridization is the main reason why the monolayer is stable, while the large $\pi$ bond stemming from their half-filled $p_z$ orbitals further strengthen the stability and make the layer keep in a plane. For Mn atom, it is coordinated by four N atoms and localized at the center of N approximate square. Apart from Mn-N coordination bond, there exist $\pi$-$d$ conjugation between $\pi$ bond of N-C framework and Mn $d_{xz}$ and $d_{yz}$ orbitals, which leads to larger $\pi$ bond extending to the overall planar monolayer. These bonding characters maintain the planarity and stability of the Mn$_2$N$_6$C$_6$ monolayer.

To clarify the structural stability of Mn$_2$N$_6$C$_6$ monolayer, we perform the calculations of formation energy, phonon spectra, molecular dynamics simulations. The formation energy $E_{form}$ is defined by $E_{form} = \frac{1}{M} (E_{tot} - 2E_{Mn} - 3E_{N_2} - 6E_C) = 0.107$ eV for Mn$_2$N$_6$C$_6$, in which $E_{tot}$, $E_{Mn}$, $E_{N_2}$, and $E_C$ are the total energy of Mn$_2$N$_6$C$_6$, bulk metal energy per atom, nitrogen molecule energy, graphene energy per atom, respectively. We also compute the formation energy of g-C$_3$N$_4$ in terms of the above method and the value is 0.35 eV. From the viewpoint of formation energy, the planar structure of Mn$_2$N$_6$C$_6$ is more stable than g-C$_3$N$_4$ that has already been synthesized in experiments [36]. The phonon spectra of Mn$_2$N$_6$C$_6$ structure is calculated in ferromagnetic order, shown in Fig. 2(a). No imaginary frequency mode
As shown in Fig. near Fermi energy are mainly from the N and Mn atoms, which indicate that the electronic states are fully spin-polarized and make a main contribution to the electronic correlation of transition metal compounds. The advantage of Hubbard U value is difficult to determine because it is not identical for different compounds. To avoid its disadvantage, M. Cococcioni and S. de Gironcoli develop a self-consistent approach to estimate the U parameter \[ U \] by the HSE hybridized functional calculations \[ \text{HSE} \], which is a more precise method than pure PBE functionals method to describe the electronic correlation of transition metal compounds. The electronic structure of \( \text{Mn}_2\text{N}_6\text{C}_6 \) is studied by the GGA + U calculations, which is a more precise method than pure PBE functionals method to describe the electronic correlation of transition metal compounds. The advantage of GGA + U method is that Hubbard U has a clear physical significance, while the disadvantage is that Hubbard U is difficult to determine because it is not identical for different compounds. To avoid its disadvantage, M. Cococcioni and S. de Gironcoli develop a self-consistent approach to estimate the U parameter \[ U \], and the method is contained in the example category in the Vaspwiki website. By this method, the Hubbard U is derived for the \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer, \( U = \chi^{-1} - \chi_0^{-1} \approx \left( \frac{\partial N^{\text{SCF}}}{\partial \gamma} \right)^{-1} - \left( \frac{\partial N^{\text{SCF}}}{\partial \gamma} \right)^{-1} = \frac{\pi_{13}}{13} - \frac{\pi_{81}}{81} = 4.88 \text{ eV} \). Fig. 3(a) shows the total density of states of \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer and the density of states projected on C, N, and Mn atoms, which indicate that the electronic states near Fermi energy are mainly from the N and Mn atoms. As shown in Fig. 3(b), the \( d_{xz} \), \( d_{yz} \), and \( d_{yz} \) orbitals are fully spin-polarized and make a main contribution to the large moment, while the \( d_{yz} \) and \( d_{xy} \) states have partial and very small contributions. The moment of Mn atom reaches up to 3.6 \( \mu_B \). Since N atom is directly connected to Mn atom, its 2p states are affected by the polarized \( d \) electrons and some spin polarization is induced. In addition, the N s, \( p_x \), \( p_y \) orbitals and Mn \( d_{xy} \) orbital are distributed in the similar energy range (not shown), corresponding to the \( sp^2 \) hybridization and the N-Mn coordination bond, which make up the framework of \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer. N \( p_z \), C \( p_z \), Mn \( d_{xz} \) and \( d_{yz} \) states have obvious overlap in their energy ranges, which is closely related to \( \pi \) conjugation between N and C atoms and the \( \pi - d \) conjugation between N and Mn atoms. The \( \pi \) and \( \pi - d \) conjugations play a key role in maintaining the planarity of \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer.

As for the magnetism of \( \text{Mn}_2\text{N}_6\text{C}_6 \) layer, we first pay attention to the magnetic coupling between two Mn moments in a dimer in \( \text{Mn}_2\text{N}_6\text{C}_6 \) layer. The two Mn moments can be aligned in the same or opposite direction. The energy for parallel alignment is 56.4 meV lower than that for antiparallel case, which indicates that there is strong ferromagnetic interaction in the dimer. The angle of Mn-N-Mn in \( \text{Mn}_2\text{N}_6\text{C}_6 \) is 81.7°, close to 90°. According to the Goodenough-Kanamori-Anderson (GKA) rules \[ 42, 43 \], when the angle of cation-anion-cation is about 90° the superexchange interaction favors ferromagnetic alignment. Consequently, the dimer of Mn atom can be regarded as a lattice point whose moment and magnetic anisotropy energy are the sum of the anisotropy energy and magnetic moment of two Mn atoms. Next, we demonstrate that the ferromagnetic order is the magnetic ground state of \( \text{Mn}_2\text{N}_6\text{C}_6 \) layer. The ferromagnetic order (FM), antiferromagnetic order I (AFM-I), and antiferromagnetic order II (AFM-II) are sketched in Fig. 4. There, the red and blue arrows mean the direction of total moment of a dimer. For each formula unit cell, the energies of AFM-I and AFM-II states are 74.4 meV and 148.2 meV higher than FM energy. We also carry out the HSE hybridized functional calculations \[ 44 \] to examine the energy order of FM, AFM-I, and AFM-II states, and the ferromagnetic ground state of \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer is confirmed.

FIG. 2. (a) Phonon spectra of \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer; (b) Total energy evolution of \( \text{Mn}_2\text{N}_6\text{C}_6 \) with respect to time in molecular dynamics simulation. The insets are the top and side views of final configurations for \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer at 1000 K after 5 ps.

FIG. 3. (a) Total density of state of \( \text{Mn}_2\text{N}_6\text{C}_6 \) and the density of states projected on C, N, and Mn atomic orbitals. (b) Density of states projected on five 3d suborbitals of Mn atom. Fermi energy is marked by the vertical dashed line.
On account of the existence of large local moments in \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer, we use Ising model to describe the magnetic interactions among lattice points, which is the simplest model to show a magnetic phase transition [10, 23, 45]. The Hamiltonian is shown below,

\[
H = \sum_{\langle i,j \rangle} J_1 S_i S_j + \sum_{\langle i,j' \rangle} J_2 S_i S_{j'}, \tag{1}
\]

where \( j \) and \( j' \) denote the neighbors of \( i \) site along different direction, and \( E_{FM}, E_{AFM-I}, \) and \( E_{AFM-II} \) are the energies of FM, AFM-I, and AFM-II orders per formula cell. In terms of the formulas 2, the exchange couplings \( J_1 \) and \( J_2 \) between two neighboring dimers are \(-37.04\) meV/\( S^2 \) and \(-0.18\) meV/\( S^2 \) [46].

\[
J_1 = \frac{1}{4}(E_{FM} - E_{AFM-II}),
\]

\[
J_2 = \frac{1}{4}(E_{FM} + E_{AFM-II} - 2E_{AFM-I}) \tag{2}
\]

The spontaneous magnetization \( (M) \) and specific heat \( (C_v) \) with respect to temperature are plotted in Fig. 5(a), and the Curie temperature of \( \text{Mn}_2\text{N}_6\text{C}_6 \) is determined with Monte Carlo method to be 974 K. If we ignore \( J_2 \) and just focus on \( J_1 \), the magnetic interactions in \( \text{Mn}_2\text{N}_6\text{C}_6 \) layer can be regarded as a 2D square lattice. Its Curie temperature can be estimated by the analytical solution of Ising model on square lattice, namely, \( T_c = 2J_1/ln(1 + \sqrt{2}) = 2.269 \times 37.04 \times 11.6 = 974.8 \) K. The values of Curie temperature with two methods are consistent with each other.

Due to the small magnetic anisotropy in real 2D ferromagnetic materials, Curie temperature is usually overestimated by Ising model. Then, we turn to Heisenberg model, which is more precise model and has been successfully used to estimate the Curie temperature of \( \text{CrI}_3 \) and other synthesized ferromagnetic 2D materials [23, 47]. For example, the calculated Curie temperature of 42 K is very close to the experimental value of 45 K in 2D ferromagnetic \( \text{CrI}_3 \) layer [48]. The Hamiltonian of Heisenberg model is defined as

\[
H = \sum_{\langle ij \rangle} J_1 S_i S_j + \sum_{\langle i'j' \rangle} J_2 S_i S_{j'} + A \sum_{i} (S_i^z)^2, \tag{3}
\]

in which the symbol \( j \) and \( j' \) represent the neighboring sites of \( i \) site in the distorted triangle lattice, and \( \alpha \) is coordinate component \( x, y, \) or \( z \). \( A \) is the single-site magnetic anisotropic energy. We perform the GGA + U + SOC calculations with the spin along (1 0 0), (0 1 0), and (0 0 1) axis for FM, AFM-I, and AFM-II magnetic orders, and the magnetic exchange interactions can be derived from these energy differences. The exchange couplings \( J_{1x}, J_{1y}, J_{1z}, J_{2x}, J_{2y}, \) and \( J_{2z} \) are -36.08, -36.10, -36.09, 0.07, 0.10, and 0.09 meV/\( S^2 \), respectively, while the single-site magnetic anisotropic energy is 0.765 meV/\( S^2 \) with easy axis normal to \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer. Fig. 5(b) displays the variation of magnetic moment and the specific heat with temperature for \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer, which gives the Curie temperature of 272 K. If the superexchange couplings between two more distant sites are taken into account, the critical temperature is 270.9 K, which manifests the reliability of the above Curie temperature derived from \( J_1 \) and \( J_2 \). The ferromagnetic critical temperature is much lower than 974 K predicted based on Ising model, indicating that Ising model significantly overestimate the Curie temperature of \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer especially in the case of small magnetic anisotropy. Yilv Guo et al summarized the recent progress of ferromagnetic 2D materials in their review article [23], and the Curie temperatures predicted by Ising model and Heisenberg model were listed in Table 1 in Ref. 23, in which the temperature from Ising model is underestimated. On the other hand, among 44 kinds of ferromagnetic 2D materials listed in Ref 23, the highest Curie temperature predicted based on Heisenberg model is 261 K, which indicates that \( \text{Mn}_2\text{N}_6\text{C}_6 \) monolayer with
Curie temperature of 272 K is a near-room-temperature ferromagnetic 2D material.

**CONCLUSION**

In summary, by the first-principles calculations, we propose an effective approach to realize the high-temperature ferromagnetism in 2D materials. Namely, two magnetic ions are gathered together to form a ferromagnetic dimer, which acts as one lattice point and has twice moment of single magnetic atom. Based on the idea, we design the Mn$_2$N$_6$C$_6$ monolayer, in which two Mn atoms in a Mn$_2$N$_6$ moiety are considered as a dimer and the distance between two dimers is short. Its structural stability is demonstrated by the phonon spectra and molecular dynamics calculations and the bonding characters are analyzed. Then, we compute the critical temperature based on Heisenberg model with Monte Carlo simulation method, and the result manifest that Mn$_2$N$_6$C$_6$ monolayer is a near-room-temperature ferromagnetic 2D material with Curie temperatures of 272 K. The example of Mn$_2$N$_6$C$_6$ monolayer is a powerful evidence to verify the feasibility of our proposed approach.

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1. K. S. Novoselov, *Science* **306**, 666 (2004).

2. L. Song, L. Ci, H. Lu, P. B. Sorokin, C. Jin, J. Ni, A. G. Kvasnhin, D. G. Kvasnhin, J. Lou, B. I. Yakobson, and P. M. Ajayan, *Nano Letters* **10**, 3200 (2010).

3. B. Lalmi, H. Oughaddou, H. Enriquez, A. Kara, S. Vizzini, B. Ealet, and B. Aufray, *Applied Physics Letters* **97**, 223109 (2010).

4. A. J. Mannix, X.-F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest, M. J. Yacaman, A. Ponce, A. R. Oganov, M. C. Hersam, and N. P. Guisinger, *Science* **350**, 1513 (2015).

5. S. Saxena, R. P. Chaudhary, and S. Shukla, *Scientific Reports* **6**, 31073 (2016).

6. J. N. Coleman, M. Lotya, A. O’Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Mohi-riarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuwissen, D. W. McComb, P. D. Nellist, and V. Nicolosi, *Science* **331**, 568 (2011).

7. M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, and M. W. Barsoum, *Advanced Materials* **23**, 4248 (2011).

8. A. N. Andriotis, E. Richter, and M. Menol, *Physical Review B* **93**, 081413(R) (2016).

9. B. Wang, S. Yuan, Y. Li, L. Shi, and J. Wang, *Nanoscale* **9**, 5577 (2017).

10. Y. Sun, Z. Zhuo, X. Wu, and J. Yang, *Nano Letters* **17**, 2771 (2017).

11. X. Tang, W. Sun, Y. Gu, C. Lu, L. Kou, and C. Chen, *Physical Review B* **99**, 045445 (2019).

12. B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgall, M. A. McGuire, D. H. Cobden, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. Xu, *Nature* **546**, 270 (2017).

13. C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang, Z. Q. Qu, R. J. Cava, S. G. Louie, J. Xia, and X. Zhang, *Nature* **546**, 265 (2017).

14. M. Bonilla, S. Kolekar, Y. Ma, H. C. Diaz, V. Kalappatil, R. Das, T. Eggers, H. R. Gutierrez, M.-h. Phan, and M. Batzill, *Nature Nanotechnology* **13**, 289 (2018).

15. W. Hu, C. Wang, H. Tan, H. Duan, G. Li, N. Li, Q. Ji, Y. Lu, Y. Wang, Z. Sun, F. Hu, and W. Yan, *Nature Communications* **12**, 1854 (2021).

16. W.-B. Zhang, Q. Qu, P. Zhu, and C.-H. Lam, *Journal of Materials Chemistry C* **3**, 12457 (2015).

17. N. Sivadas, M. W. Daniels, R. H. Swendsen, S. Okamoto, and D. Xiao, *Physical Review B* **91**, 235425 (2015).

18. J. Guan, C. Huang, K. Deng, and E. Kan, *The Journal of Physical Chemistry C* **123**, 10114 (2019).

19. S. Zheng, C. Huang, T. Yu, M. Xu, S. Zhang, H. Xu, Y. Liu, E. Kan, Y. Wang, and G. Yang, *The Journal of Physical Chemistry Letters* **10**, 2733 (2019).

20. S. Chen, F. Wu, Q. Li, H. Sun, J. Ding, C. Huang, and E. Kan, *Nanoscale* **12**, 15670 (2020).

21. B. Wang, X. Zhang, Y. Zhang, S. Yuan, Y. Guo, S. Dong, and J. Wang, *Materials Horizons* **7**, 1623 (2020).

22. D. Liu, S. Zhang, M. Gao, X.-W. Yan, and Z. Y. Xie, *Applied Physics Letters* **118**, 223104 (2021).

23. Y. Guo, B. Wang, X. Zhang, S. Yuan, L. Ma, and J. Wang, *InfoMat* **2**, 639 (2020).

24. P. Huang, P. Zhang, S. Xu, H. Wang, X. Zhang, and H. Zhang, *Nanoscale* **12**, 2309 (2020).

25. Z. Lu, B. Wang, Y. Hu, W. Liu, Y. Zhao, R. Yang, Z. Li, J. Luo, B. Chi, Z. Jiang, M. Li, S. Mu, S. Liao, J. Zhang, and X. Sun, *Angewandte Chemie* **131**, 2648 (2019).

26. Q. Q. Yuan, Z. Guo, Z. Q. Shi, H. Zhao, Z. Y. Jia, Q. Wang, J. Sun, D. Wu, and S. C. Li, *Chinese Physics Letters* **37**, 077502 (2020), arXiv:2006.00333.

27. G. Kresse and J. Hafner, *Physical Review B* **47**, 558 (1993).

28. G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).

29. J. P. Perdew, K. Burke, and M. Ernzerhof, *Physical Review Letters* **77**, 3865 (1996).

30. P. E. Blöchl, *Physical Review B* **50**, 17953 (1994).

31. M. Cococcioni and S. de Gironcoli, *Physical Review B* **71**, 035105 (2005).

32. A. Togo and I. Tanaka, *Scripta Materialia* **108**, 1 (2015).

33. G. J. Martyna, M. L. Klein, and M. Tuckerman, *The Journal of Chemical Physics* **97**, 2635 (1992).
[34] L. Liu, https://github.com/golddoushi/mcsolver (accessed Mar 25, 2021).
[35] L. Liu, S. Chen, Z. Lin, and X. Zhang, Journal of Physical Chemistry Letters 11, 7893 (2020).
[36] M. Groenewolt and M. Antonietti, Advanced Materials 17, 1789 (2005).
[37] H. Fei, J. Dong, Y. Feng, C. S. Allen, C. Wan, B. Volosskiy, M. Li, Z. Zhao, Y. Wang, H. Sun, P. An, W. Chen, Z. Guo, C. Lee, D. Chen, I. Shakir, M. Liu, T. Hu, Y. Li, A. I. Kirkland, X. Duan, and Y. Huang, Nature Catalysis 1, 63 (2018).
[38] L. Zhao, Y. Zhang, L.-B. Huang, X.-Z. Liu, Q.-H. Zhang, C. He, Z.-Y. Wu, L.-J. Zhang, J. Wu, W. Yang, L. Gu, J.-S. Hu, and L.-J. Wan, Nature Communications 10, 1278 (2019).
[39] N. Zhang, T. Zhou, J. Ge, Y. Lin, Z. Du, C. Zhong, W. Wang, Q. Jiao, R. Yuan, Y. Tian, W. Chu, C. Wu, and Y. Xie, Matter 3, 509 (2020).
[40] D. Liu, S. Zhang, M. Gao, and X.-W. Yan, Physical Review B 103, 125407 (2021).
[41] D. Liu, P. Feng, M. Gao, and X.-W. Yan, Physical Review B 103, 155411 (2021).
[42] J. B. Goodenough, Physical Review 100, 564 (1955).
[43] P. W. Anderson, Physical Review 115, 2 (1959).
[44] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, The Journal of Chemical Physics 125, 224106 (2006).
[45] K. Zhao and Q. Wang, Applied Surface Science 505, 144620 (2020).
[46] F. Ma, Z.-Y. Lu, and T. Xiang, Physical Review B 78, 224517 (2008).
[47] J. Liu, Q. Sun, Y. Kawazoe, and P. Jena, Physical Chemistry Chemical Physics 18, 8777 (2016).
[48] Y. Zhang, B. Wang, Y. Guo, Q. Li, and J. Wang, Computational Materials Science 197, 110638 (2021).