JPhys Materials

Ab initio study on anisotropic thermoelectric transport in ternary pnictide KZnP

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Keywords: thermoelectricity, ab initio calculations, electron–phonon interaction

Abstract

Strongly anisotropic bands near the Fermi level via band structure engineering have been proposed to enhance thermoelectric performance in functional materials. Recent works exhibit the presence of flat-and-dispersive-band-like strong anisotropy in a class of ternary transition metal pnictides. Taking KZnP as a representative example, here we investigate the thermoelectric properties of this class of materials based on first-principles calculations and semiclassical Boltzmann transport theory. Strikingly, the calculated lattice thermal conductivity κL shows a strong anisotropy with a small value of about 5.24 (2.58) W m⁻¹K⁻¹ along the in-plane (out-of-plane) lattice direction at room temperature. Based on the electron relaxation time calculated from intensive ab initio electron–phonon interactions, a thermoelectric figure of merit zT of 0.32 is predicted for n-type doped KZnP, about two times lower than the value estimated by the constant relaxation time approximation from deformation potential theory. Nanostructures with the characteristic length shorter than 13 nm can reduce the κL by 40%, enhancing zT to 0.52 along the c axis direction. This work supports that KZnP is a potential candidate for thermoelectric applications.

1. Introduction

Over the past decade, research focus on thermoelectric materials has increased drastically because of their capacity of direct and reversible conversion between thermal and electrical energy via the Seebeck and Peltier effect, which provides a promising route to convert waste heat into electricity [1–5]. The conversion efficiency of thermoelectric materials is limited by the dimensionless figure of merit (ZT), defined as $ZT = \frac{S^2\sigma T}{k_L + k_e}$, where $S$, $\sigma$, $T$, $k_L$ and $k_e$ are the Seebeck coefficient, the electrical conductivity, the absolute temperature, the lattice and the electronic thermal conductivity, respectively. Hence, to improve the thermoelectric performance, a high thermoelectric power factor ($S^2\sigma$) and a low thermal conductivity ($k_L + k_e$) are required simultaneously. However, the coupling of transport coefficients brings difficulty in meeting this demand [2].

Hicks and Dresselhaus suggested a promising avenue to overcome the conundrum by utilizing the low-dimensional structures, such as semiconductor quantum wells, and quantum dots [6]. A drastic increase in Seebeck coefficient was observed experimentally in Bi nanowires [7] and two-dimensional electron gas in SrTiO₃ [8]. In more details, the Mahan-Sofo theory [9] unravels the enhancement of $S$ from the view of local increase in electron density of states (DOS) [10]. However, the two factors to increase $S$ seem to be of conflicting: sharp DOS is associated with flat energy bands, while high carrier velocities require highly dispersive ones. Alternatively, many attempts via ‘band structure engineering’ have been made to combine these two conflicting
factors. For instance, the power factors 4–5 times larger than PbTe or Bi2Te3 was obtained by engineering the appearance of Fe $e_g$ states at the bottom of the conduction bands in Fe$_2$YZ full Heusler compounds [11]. Strong band dispersion along only one direction by designing a ‘phonon glass-electron crystal’ has been proved to be effective to enhance thermoelectric performance [12]. Apparently, coexistence of flat and highly dispersive bands near the Fermi level offers a very promising avenue for exploring materials with desired properties, since a small effective mass in one direction benefits the carrier mobility and hence the electrical conductivity, while a large effective mass along the other direction contributes to an overall large DOS and large Seebeck coefficient. Recent works show the natural coexistence of the ‘flat-and-dispersive’ band structure in XYZ ($X = Li, Na, K$; $Y = Zn, Cd, Hg; Z = P, As, Sb, Bi$) ternary transition metal pnictide compounds. Thus, considering the above specific band structure and the diverse number of atomic configurations, these compounds hold promise for excellent thermoelectric performance.

In this work, we investigate thermoelectric transport properties of $n$-type KZnP with the $P6_3/mmc$ symmetry group based on ab initio calculations. We first calculate the lattice thermal conductivity of KZnP by solving the phonon Boltzmann transport equation (BTE) self-consistently. Detailed contributions to $k_f$ from acoustic and optical phonon modes and the mean free path (MFP) distributions are analyzed for guiding the further reduction of $k_f$ with all-scale hierarchical architecuting. The energy dependent electron relaxation time is accurately evaluated from the ultra-dense electron configurations, these compounds hold promise for excellent thermoelectric performance.

2. Methods

We performed ab initio calculations within the framework of density functional theory, as implemented in QUANTUM ESPRESSO package [13]. Projector augmented wave pseudopotential was employed to model the electron–ion interaction and the exchange-correlation function is in the form of generalized gradient approximation with Perdew–Burke–Ernzerhof (PBE) [14]. The kinetic energy cut-off and the charge density cut-off of the plane wave basis were chosen to be 100 Ry and 600 Ry respectively. The Methfessel-Paxton smearing technique of width 0.01 Ry was used [15]. The self-consistent electron density was evaluated on a $16 \times 16 \times 8$ $k$-point grid. The lattice constants after full geometry optimization were adopted. The HSE06 calculations were also carried out to correct the energy band gap and thermoelectric parameters.

Phonon BTE together with the interatomic force constants (IFCs) were applied to calculate lattice thermal conductivity via an iterative solution in ShengBTE package [16], where the second-order (third-order) IFCs are calculated within the $6 \times 6 \times 3 (4 \times 4 \times 2)$ supercells [17]. The anharmonic interactions up to the fifth nearest neighbors (the corresponding cutoff is 0.667 nm) [18], which give rise to 540 displaced structures in total, were included to calculate the anharmonic IFCs with only $\Gamma$ point sampling in the Brillouin zone (BZ) to ensure the convergence of lattice thermal conductivity. At last, a $q$-mesh of $18 \times 18 \times 9$ was selected to simulate the $q$ space integration for ShengBTE calculations.

The energy dependent electron relaxation time is accurately evaluated from the ultra-dense electron–phonon coupling matrix elements via the maximally localized Wannier functions [19, 20] as implemented in the electron–phonon Wannier package [21, 22]. Twelve orbitals in total (one $s$ orbital from each K, Zn and P atom and three $p$ orbitals from each P atom; each unit-cell contains two K, Zn, P atoms) have been used to construct real space Hamiltonian in the Wannier basis. The electron self-energy $\Sigma^{\text{el}}$ for band $n$ and state $k$ was obtained by initially using a coarse $6 \times 6 \times 3$ $k$ and $q$ mesh, and then interpolating to a dense mesh of $36 \times 36 \times 18$. The interpolated Wannier electron band structure and phonon dispersion relations agree well with those obtained directly from ab initio calculations. Finally, the electronic transport coefficients can be calculated by using semiclassical Boltzmann theory (see detailed expression in the supplementary information (SI) available online at stacks.iop.org/JPMATER/2/024001/mmedia) and the rigid band approach [23].

3. Results and discussion

3.1. Atomic structure and phonon transport

The ternary transition metal pnictide class XYZ, which is structurally related to Heuslers class, can be viewed as $X$ stuffed ($X = K$) graphene $YZ$ lattice consisting of alternating late transition metals $Y$ (Zn, Cd) and main group elements $Z$ ($P$, $As$) [24], as shown in figure 1. Here we take KZnP as an example. The formation energy per unit cell of KZnP with the symmetry group of $P6_3/mmc$ is $-0.46$ eV, which is 58 meV lower than that of $K_2ZnP_2$ with
the symmetry group of $R3m$ [25]. The intermediate ZnP layer is similar to graphene with breaking sublattice symmetry, and the adjacent ZnP layers are AB stacked intercalated by K in between. The optimized lattice constants are $a \sim 4.10$ Å and $c \sim 10.27$ Å using the PBE functional, which is consistent with the previous calculations [25] and experimental results [26].

The calculated phonon spectrum of bulk KZnP is plotted in figure 2(a). The absence of imaginary modes in the entire BZ is a significant confirmation that bulk KZnP is thermodynamically stable. Due to the existence of six atoms in the primitive cell of bulk KZnP, there are eighteen phonon branches including three acoustic and fifteen optical branches. All three acoustic branches are well described by a linear dispersion around $\Gamma$, unlike those in two-dimensional materials, where low-frequency out-of-plane acoustic (ZA) branch is quadratic [18, 27–29]. The ZA and transverse acoustic branches are nearly degenerated near the zone center ($q \rightarrow 0$). It is obvious that optical branches open up a gap, and many low optical modes are highly hybridized with the three acoustic modes, similar to the previous results for GaSe-class materials [30]. The phonon DOS shown in figure 2(b) indicates that the opened gap originates from the P atoms of the intermediate ZnP layer, which contribute mainly to the high frequency phonon modes ($\sim$300–350 cm$^{-1}$). In addition, the intermediate frequency phonons are mainly afforded by Zn atoms, thus the Zn atoms act as a bridge to make more phonons satisfy phonon scattering conditions, and then play a crucial role in anharmonic three-phonon scattering processes and decreasing lattice thermal conductivity.

Figure 2(c) shows the self-consistently (via iterative methods) calculated lattice thermal conductivity of bulk KZnP along $a/b$ axis and $c$ axis directions, which is 21.2% and 2.7% larger than the values from relaxation time approximation (RTA), respectively. The detailed values of the lattice thermal conductivity calculated via iterative method and RTA are as follows: at 300 K, those along $a/b$ direction are 5.4 W m$^{-1}$K$^{-1}$ and 4.25 W m$^{-1}$K$^{-1}$, respectively; those along $c$ direction are 2.58 W m$^{-1}$K$^{-1}$ and 2.51 W m$^{-1}$K$^{-1}$, respectively. These results indicate that the three-phonon processes play an important role along the $a/b$ axis direction, while Umklapp scattering is strong along the $c$ axis direction [16]. According to the hexagonal symmetry of KZnP, the lattice thermal conductivity is isotropic in the $ab$ plane. At room temperature, the $\kappa_2$ along $a/b$ axis and $c$ axis are about 5.24 and 2.58 W m$^{-1}$K$^{-1}$, respectively, indicating a strong anisotropy with a factor of $\sim$2.09 ($a/b$ axis $\kappa_2$ versus $c$ axis $\kappa_2$). The significant anisotropy can be attributed to different three-phonon scattering mechanism along the $a/b$ and $c$ axis, as mentioned above. The anisotropy ratio of $a/c$ is comparable to that of bulk $\alpha$-HgS with a factor of 1.8 [31], that of bulk SnSe crystal with a factor of 2–2.5 [32], and that of some 2D materials (WTe$_2$ [18] and black phosphorene [33, 34]). As the temperature increases, the anisotropy ratio decreases monotonically from 2.09 at 300 K to 1.94 at 1200 K. In addition, natural isotope scattering (see details of the isotope scattering term in SI) can lead to a modest reduction in $\kappa_2$, e.g. 6.1% and 8.8% along $a/b$ and $c$ axis at 300 K, respectively.
Furthermore, we also show the calculated percentages of $a/b$ axis and $c$ axis thermal conductivities to the corresponding total values, decomposed into acoustic and optical phonon branches (figure 2(d)). The $a/b$ axis thermal conductivities are near equally attributed to three acoustic and all optical branches. However, the optical branches play a dominant role in the $c$ axis thermal conductivity with a contribution of near 77%, even larger than that of SnSe crystals with a value of 60% [32]. High frequency modes (300–350 cm$^{-1}$) from P atoms contribute 23% (figure S1 in SI). Assuming that the optical phonon contribution is completely suppressed by point-defect scattering [23], $\kappa_L$ at 300 K would be reduced to 2.43 and 0.59 W m$^{-1}$K$^{-1}$ along the $a/b$ and $c$ axis, respectively. On the other hand, the normalized thermal conductivity integration with respect to the MFP was also analyzed for guiding further reduction of $\kappa_L$ with all-scale hierarchical architecturing [35], as shown in figure 2(c). The $\kappa_L$ integration keeps increasing as MFP increases, until reaching the thermodynamic limit. At room temperature, heat is mainly carried by phonons with MFPs ranging from 1 to 100 nm and the MFP values

Figure 2. Phonon transport properties of KZnP. (a) Phonon dispersion of KZnP. (b) Phonon density of states (PDOS) of KZnP. Total PDOS (gray rectangle) is the total contribution from those of K (green lines), Zn (red lines) and P (blue lines) atoms. (c) Lattice thermal conductivity $\kappa_L$ of KZnP as a function of temperature. The inset shows the normalized $\kappa_L$ integration for KZnP with respect to the phonon MFP along different directions. The red and black lines denote $a/b$ and $c$ axis, respectively. (d) The contribution of acoustic (solid symbols) and optical (hollow symbols) branches to total lattice thermal conductivity of KZnP as a function of temperature along $a/b$ (black lines) and $c$ (red lines) axis, respectively.
corresponding to 60% $\kappa_L$ accumulation are 15 nm (13 nm) along the $a/b$ ($c$) axis. The phonon MFPs of bulk KZnP are obviously shorter than that of PbSe and PbTe and comparable to that of $\alpha$-HgS and SnSe.

3.2. Electronic properties and *ab initio* electron–phonon scattering

Next, we focus on the electronic properties of KZnP, as presented in figure 3(a). The $\Gamma$-point hosts a direct band gap of about 0.85 (1.57) eV based on the PBE (HSE06) calculations. Compared to the band gap of 2.0 eV calculated from the TBmBJ potential [25], the band gap predicted using HSE06 functional (1.57 eV) is underestimated. Interestingly, KZnP exhibits a ‘flat-and-dispersive’ band character that the valence band is nearly flat along the $c$ axis direction but highly dispersive in the $ab$ plane, while the conduction band is significantly dispersive along all directions. This special band structure has been shown to enhance the thermoelectric performance effectively in Fe$_2$YZ full Heusler compounds [11], phonon–glass crystals [12], $\alpha$-HgS [31], SrTiO$_3$ [23, 36], etc. Obviously, the effective mass of the free carriers in KZnP is highly anisotropic because it is proportional to the inverse of the curvature of the band dispersion, as illustrated in real space in figures 3(b), (c) for holes and electrons, respectively. For example, the distribution of effective mass of holes

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**Figure 3.** Electronic properties of KZnP. (a) Electronic band structure of KZnP calculated by PBE (black lines) and HSE06 (red circles), respectively. The Fermi level is set at the valence band maximum. (b), (c) The spatial dependent carrier effective mass of hole (b) at the valence band maximum and electron (c) at the conduction band minimum, respectively.
shows an ‘8’ shape with the value of 0.51 $m_e$ ($m_e$ is the bare electron mass) in $ab$ plane and 5.11 $m_e$ along the $c$ axis direction. The effective mass of electrons has a slightly weak anisotropy but a smaller value compared with that of holes, which is 0.1 $m_e$ in $ab$ plane and 0.28 $m_e$ along the $c$ axis direction.

Generally speaking, the carrier relaxation time is the only parameter in the framework of semiclassical Boltzmann theory when dealing with the electronic transport properties. The DP theory, as the simplest method to simplify the e-ph interaction, is widely applied to approximate the carrier relaxation time and mobility in previous studies [37]. In fact, there is increasing evidence in phosphorene [23], MoS$_2$ [38], GaAs [39, 40], GaN [41] that DP theory overestimates the carrier relaxation time and the $zT$ value. For example, the DP theory gives the $zT$ value of phosphorene to be close to 1 [33], which is about an order of magnitude larger than that calculated with $ab$ initio scattering methods [23]. Here, the energy dependent carrier relaxation time $\tau_{nk}$ is computed from the imaginary part of the self-energy $\text{Im}(\Sigma_{nk})$ as $\tau_{nk}^{-1} = 2\text{Im}(\Sigma_{nk})/\hbar$, assuming electrons are scattered by phonons only in perfect crystalline samples since electron–electron scattering is negligible compared with e-ph scattering [42]. Figure 4(a) shows the imaginary part of the e-ph self-energies at 300 K. Our calculations show that the electron self-energies of the conduction band are much smaller than those of the valence band, implying a larger electron relaxation time and thus higher electron mobility in the conduction band. At 300 K, the maximum relaxation time around the conduction band maximum (CBM) is about 9.8 fs, which is much larger than the value of only 1.1 fs near the valence band minimum (VBM). In contrast, DP theory roughly estimates a constant relaxation time of VBM and CBM at 300 K to be 39.5 (237.9) and 678.8 (592.5) fs along $ab$ ($c$) axis direction, respectively. The DP parameters are presented in the supporting information.

To gain further insight into e-ph scattering, we carry out a quantitative analysis of the contributions from the individual modes to the total e-ph self-energies, as shown in figure 4(b). For the whole energy range, the electron self-energies are dominated by all optical modes with a contribution about 40%–50%, indicating that the contributions from optical phonons cannot be neglected. Such a large contribution from optical phonons is also found in phosphorene [23], MoS$_2$ [38], GaAs [39], which highlights the limitations of DP theory to study the e-ph scattering approximately. Additionally, the ZA mode possess the greatest self-energies among three acoustic modes with a contribution of about 30% for the conduction band, 10%–20% larger than that of longitudinal acoustic (LA) mode.

3.3. Thermoelectric performance

In order to obtain the authentic thermoelectric transport performance, rigid band shift, also named scissors shift, is applied to correct the potential effects of the underestimated band gap on thermoelectric parameters. Our calculations (figure S2 in SI) show that HSE corrected band gap can dramatically change the thermoelectric parameters only at very low doping concentration, however it generates negligible effects on thermoelectric parameters if the carrier doping concentration is larger than $1.0 \times 10^{18}$ cm$^{-3}$ (1.5 $\times 10^{-4}$ $e$ per unit-cell). Here, we discuss the results calculated from HSE functionals in the following. Owing to the much higher electron...
relaxation time of the conduction band and the lower lattice thermal conductivity along \( c \) axis, the best thermoelectric performance is expected along the \( c \) axis of bulk KZnP with \( n \)-type doping.

Figure 5(a) shows the Seebeck coefficient \( S \) calculated from \textit{ab initio} e-ph scattering as a function of carrier concentration \( n \) along the \( c \) axis direction for \( n \)-type KZnP at the temperature \( T \) from 300 to 1200 K. A negative \( S \) means \( n \)-type doping, while a positive \( S \) represents \( p \)-type doping. Obviously, the \(-S\) increases with temperature \( T \) at the same doping concentration \( n \), and decrease with \( n \) at the same \( T \), being consistent with the tendency observed in most of semiconducting thermoelectric materials [4, 5]. The \(-S\) along \( c \) axis direction at \( n \sim 3.2 \times 10^{20} \, \text{cm}^{-3} \) are in the range of 123.5–195.9 \( \mu \text{V K}^{-1} \) as \( T \) increases from 300 to 1200 K. The corresponding thermoelectric parameters along \( ab \) axis direction is available in supporting information. The calculated Seebeck coefficients are weakly anisotropic \( (S_{aa} = S_{bb} \neq S_{cc}) \). For instance, the Seebeck coefficient at 300 K along \( ab \) axis and \( c \) axis direction for KZnP are 108.3 and 123.5 \( \mu \text{V K}^{-1} \), respectively, at the optimal doping concentration \( n \).

Because carrier doping generally benefits the electrical conductivity (figure S2 in SI) while deteriorating the Seebeck coefficient, \( zT \) will first increase and then decrease with the carrier concentration, therefore leading to an optimal value [23], as shown in figure 5(b). At moderate carrier concentration of \( n \sim 1.6 \times 10^{20} \, \text{cm}^{-3} \), corresponding to the electron doping level of \( \sim 0.024 \) \( e \) per unit cell (six atoms total), the maximum \( zT \) of 0.03 is achieved at 300 K. Strikingly, a highest \( zT \) can exceed 0.32 at carrier concentration of \( n \sim 3.2 \times 10^{20} \, \text{cm}^{-3} \) at 1200 K. In addition, it is found that nanoscale grain boundaries or precipitates can significantly scatter phonons [43], thus improving the thermoelectric performance effectively. This is based on the fact that the introduced nanostructures can block the phonon flow while leaving the electrons intact, since the MFPs of phonons are much longer than that of electrons [44]. Here, nanostructures with the characteristic length shorter than 13 nm can reduce the \( \kappa_L \) 40% along the \( c \) axis direction. As a result, the optimal...
zT at 300 K can be improved to 0.04 in n-type KZnP along the c axis direction, and can further reach 0.52 if the temperature is above 1200 K. It should be noted that the above ZT values are for impurity-free KZnP compounds and should be regarded as an upper limit for the thermoelectric performance of KZnP. Although the illustrated ZT of KZnP is smaller than that of the best-known narrow band gap semiconductor (having \(ZT \approx 1\)), the performance of the lattice thermoelectric conductivity along the c direction (having \(k_L \approx 1 \text{ W m}^{-1}\text{K}^{-1}\)) is satisfactory. Thus, KZnP compounds still have a good potential for practical thermoelectric applications.

Finally, DP theory was also employed to estimate a constant carrier relaxation time of KZnP and to evaluate the Seebeck coefficient and \(zT\) value, which are compared with the \textit{ab initio} results, as shown in figures 5(c) and (d). Detailed results are presented in supporting information. The disagreement of Seebeck coefficient at the same temperature from \textit{ab initio} \(\epsilon-\phi\) scattering and DP theory can be explained by that the Seebeck coefficient is independent of relaxation time only when the relaxation time is constant [23]. Here, DP theory gives a constant time while \(\epsilon-\phi\) scattering generates an energy dependent relaxation time. Our calculations show that \(zT\) of KZnP at 300 K from DP theory is 0.17 and exceeds 0.6 at 1200 K, which is approximately two times larger than that from \textit{ab initio} \(\epsilon-\phi\) scattering calculations. The overestimated \(zT\) value from DP theory is caused by the fact that the simple DP theory does not consider the contribution from the optical phonon scatterings, which is nearly 40%–50% of the total as mentioned above. Within the same framework of DP theory, the obtained \(zT\) value is comparable to that of phosphorene (~1 at 300 K [33]), TaAs (0.6 at 900 K [45]), and NaH (0.3–1.0 at 1000 K [46]).

### 3.4. Thermoelectric performance of KZnSb and KCdAs

We also discuss the thermoelectric performance of other ternary pnictides in the same family of materials as KZnP. Besides KZnP, KCdAs and KZnSb are the members in the same family with an obvious band gap, which were studied based on the DP theory and the semiclassical Boltzmann transport theory. The thermal lattice conductivity along c axis direction has the trend of KZnP > KZnSb ≈ KCdAs, for instance the values at 300 K along c axis direction for KZnP, KZnSb and KCdAs are 2.58, 0.61 and 0.64 \(\text{W m}^{-1}\text{K}^{-1}\), respectively. However, the largest \(zT\) value turns out to be KZnP > KZnSb ≈ KCdAs. It is noted that the highest peak of obtained \(zT\) for KZnSb at 300 K (700 K) is 0.81 (0.75), being consistent with that of 0.7 at 600 K reported in [47]. Detailed results are presented in supporting information. On the whole, we can conclude that compounds in the ternary transition-metal pnictide class, especially KZnP, are good candidates for potential thermoelectric applications.

### 4. Conclusion

We have used combined \textit{ab initio} calculations and BTEs to study the thermal and electrical transport properties of n-type KZnP. We find that the phonon dispersion and the corresponding phonon DOS show that Zn atoms play a crucial role in anharmonic three-phonon scattering processes. We discover that the anisotropy factor of thermal conductivity is about two, which is mainly attributed to different three-phonon scattering mechanism, where the normal three-phonon processes play an important role along the \(ab\) axis direction while Umklapp scattering is strong along the c axis. Detailed phonon transport calculations show that optical phonon modes contribute 77% to the total lattice thermal conductivity along c axis, in which high frequency (300–350 cm\(^{-1}\)) modes from P atoms contribute 23%. It is found that nanostructures with the characteristic length shorter than 13 nm can reduce the \(\epsilon\) 40% along the c axis direction. Moreover, HSE corrected band gap generates negligible effects on thermoelectric parameters of KZnP if the doping electron number per unit cell is larger than 1.5 \(\times\) \(10^{-4}\). In a large energy range around the Fermi level, the electron self-energies are dominated by optical modes whose contribution is \(\sim 40\%–50\%\). A maximum \(zT\) of 0.32 is found from \textit{ab initio} calculations on electron–phonon scattering for n-type doped KZnP, which is twice smaller than that estimated from the DP theory. The thermoelectric performance of KZnSb and KCdAs is comparable to that of KZnP. These results indicate that KZnP class compounds are potential candidates for future thermoelectric applications.

### Acknowledgments

The authors thank Dr Dengdong Fan from Wuhan University for helpful discussions. We acknowledge financial support from the National Key Research and Development Projects of China (2016YFA0300902 and 2016YFA0202300), the National Scientific Foundation of China (11774396, 61725107, 51572290 and 11334006), and the Chinese Academy of Sciences (XDB06, XDB30000000 and XDB07030100). Jian Liu and Yinchang Zhao contributed equally to this work.
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