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Supporting Information

The stability, electronic, and photocatalytic properties of $ZnWO_4$ (010) surface determined from first-principles and thermodynamic calculations

Yonggang Wu[a,b], Jihua Zhang[c], Bingwei Long[a], Hong Zhang[a*]

[a] College of Physics, Sichuan University, Sichuan, 610065, China

[b] School of Physics and Electronic Science, Guizhou Education University, Guiyang 550018, China

[c] Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Education University, Guiyang 550018, China

E-mail: hongzhang@scu.edu.cn

1. Optical Properties

The linear optical properties can be obtained from the frequency-dependent complex dielectric function

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad [A1]$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function, respectively, and ω is the phonon energy. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function $\varepsilon(\omega)$ is calculated using the standard formulation[1]

$$\varepsilon_2(\omega) = \frac{Ve^2}{2\pi\hbar m^2\omega^2}\int d^3\mathbf{k}\sum_{n,n'} |< n\mathbf{k}|\mathbf{p}|n'\mathbf{k} >|^2 f_{n\mathbf{k}}(1 - f_{n\mathbf{k}'})\delta(E_{n\mathbf{k}} - E_{n'\mathbf{k}} - \hbar\omega) \quad [A2]$$

where V is the cell volume, $\hbar\omega$ is the energy of the incident photon, $\mathbf{p}$ is the momentum operator, $|nk>$ denotes the electronic state $\mathbf{k}$ in band n, and f_{nk} is the Fermi occupation function. The real part $\varepsilon_1(\omega)$ is related to $\varepsilon_2(\omega)$ by the Kramer–Krönig transformation. The absorption coefficient $\alpha(\omega)$ can be derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ as follows[2, 3]

$$\alpha(\omega) = \frac{\sqrt{2}\omega}{c}[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)]^{1/2} \quad [A3]$$

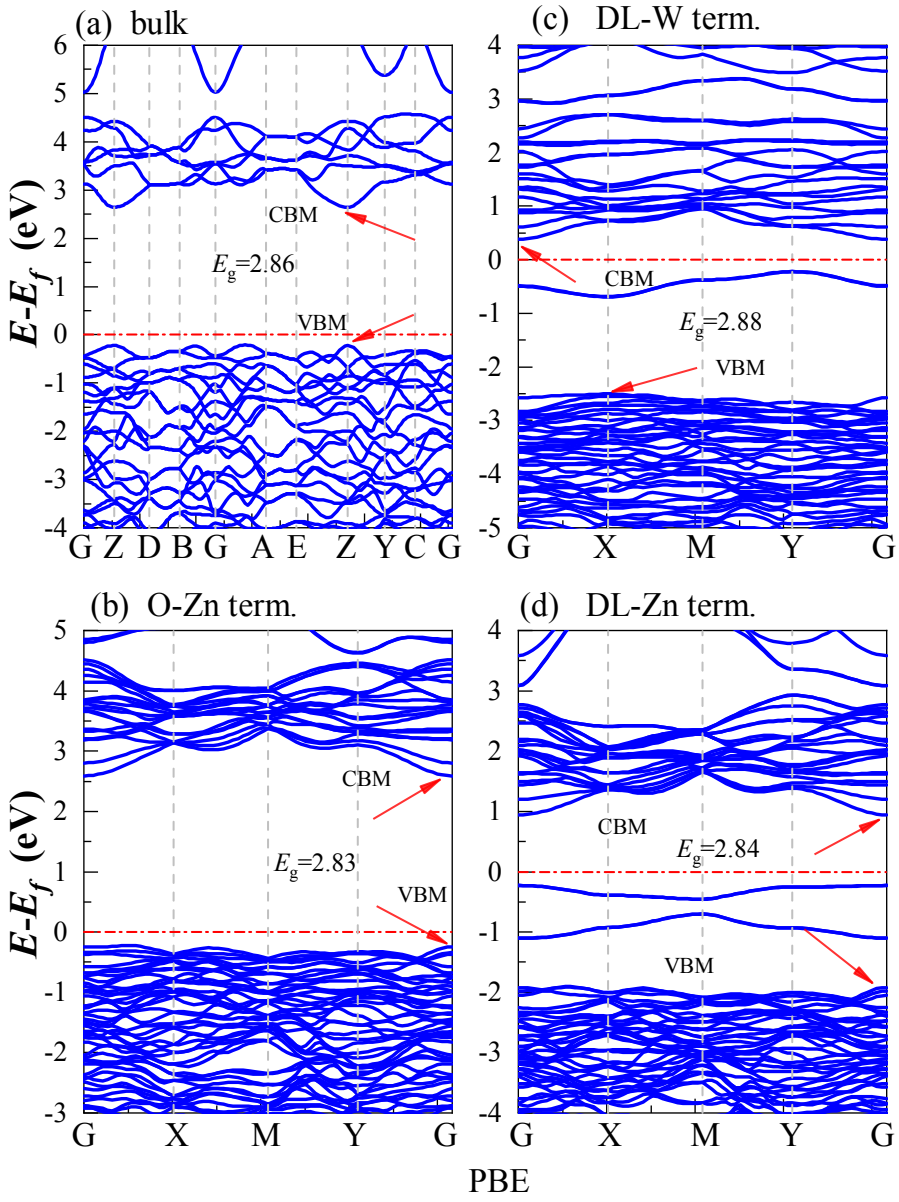


Fig. S1. The band structures of (a) bulk $ZnWO_4$ (b) O-Zn term., (c) DL-W term., and (d) DL-Zn term. for the $ZnWO_4$ (010) surface, which are obtained from the GGA-PBE calculations. The Fermi level is set to zero and indicated by a horizontal red dot-dash line.

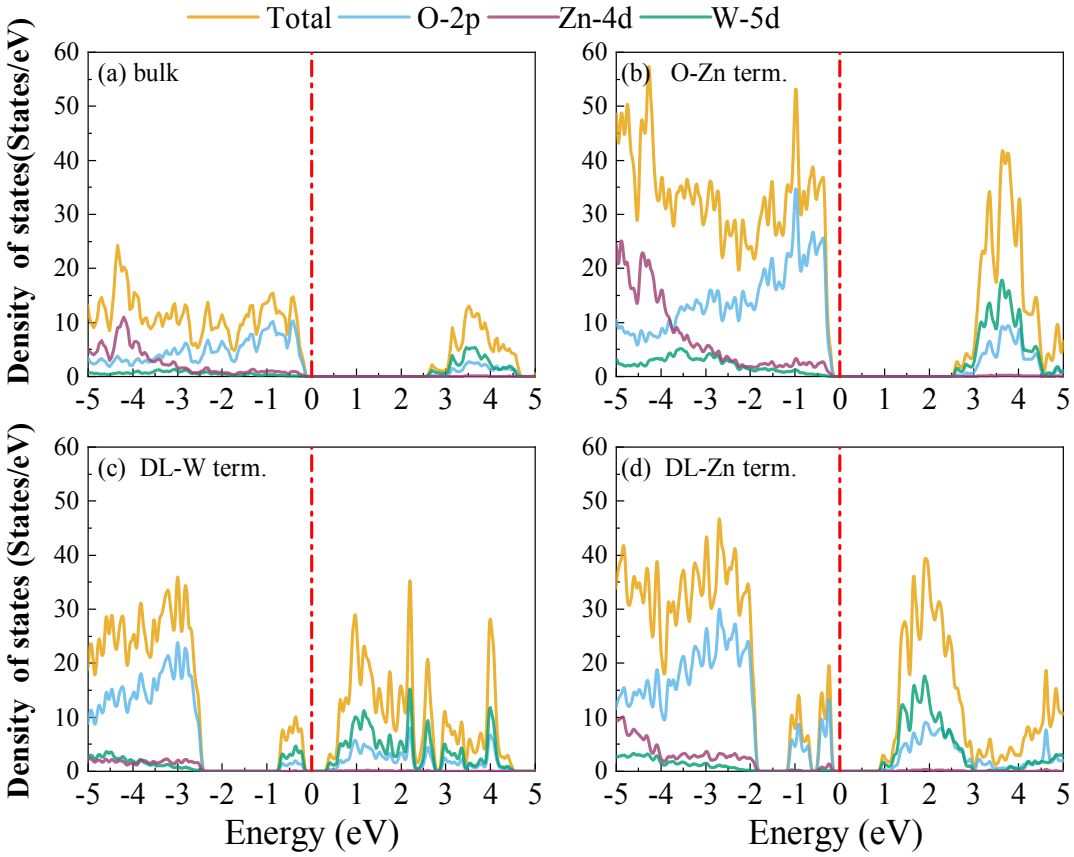
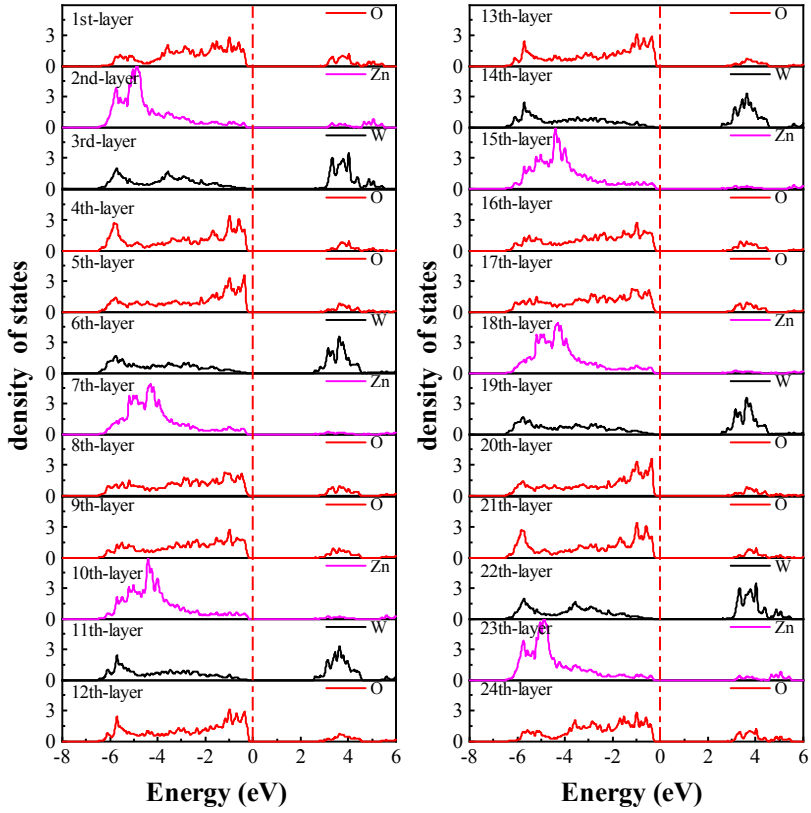
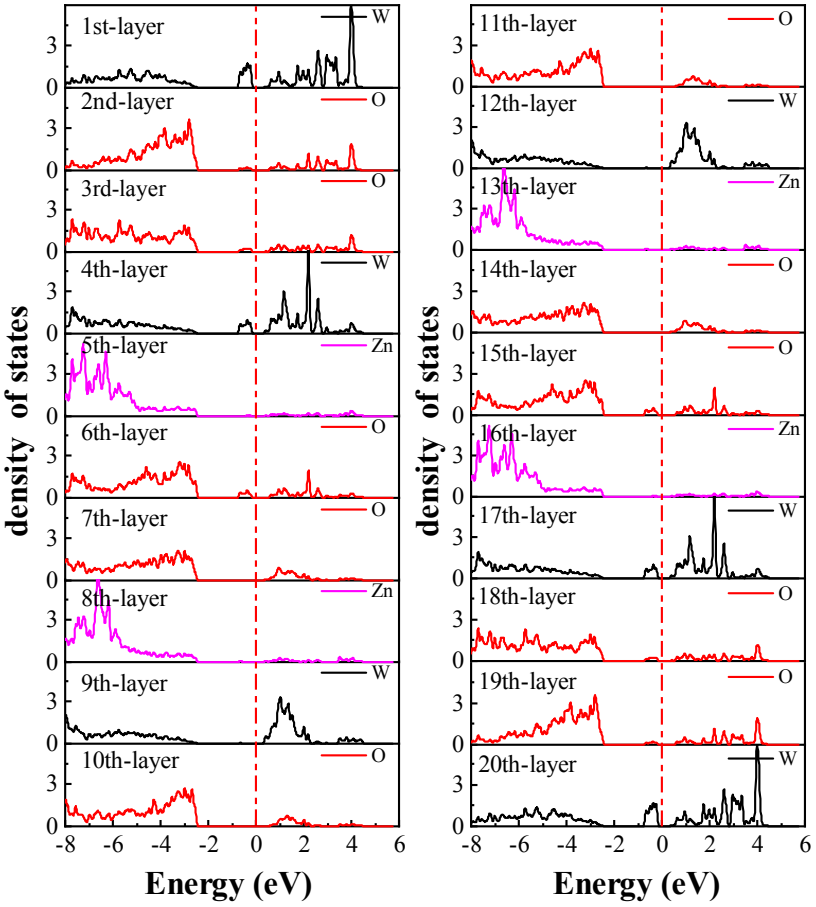


Fig. S2. The total density of states of (a) bulk $ZnWO_4$ (b) O-Zn term., (c) DL-W term., and (d) DL-Zn term., for the $ZnWO_4$ (010) surface, which are obtained from the GGA-PBE calculations. The Fermi level is set to zero and indicated by a perpendicular red dot-dash line.

(a) O-Zn term.



(c) DL-W term.



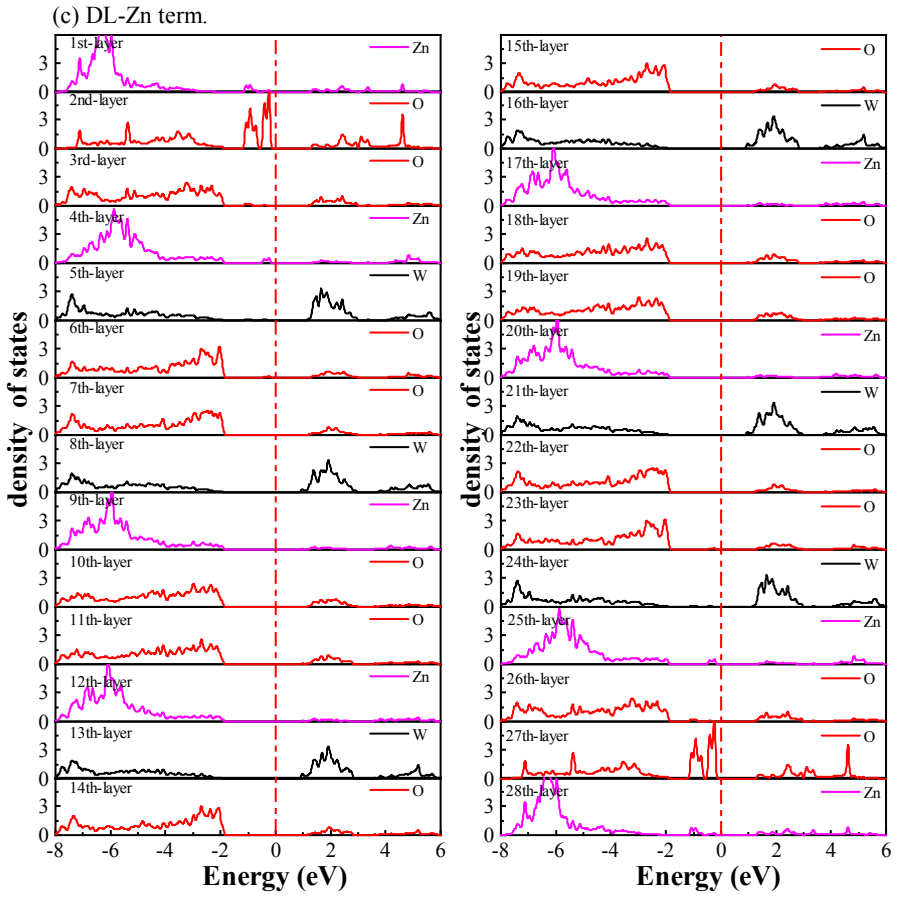


Fig. S3. The layer-resolved density of states of (a) O-Zn term., (b) DL-W term. (c) DL-Zn term., for $ZnWO_4$ (010) surfaces, which are obtained from the GGA-PBE calculations. The Fermi level is set to zero and indicated by a perpendicular red dot-dash line.

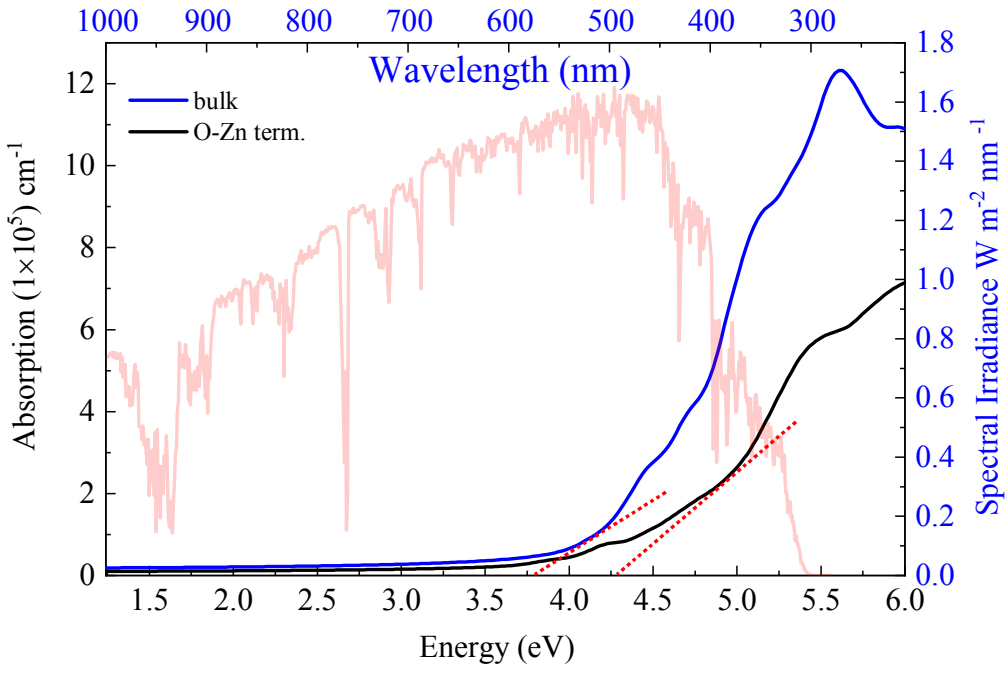


Fig. S4 Calculated the bulk ZnWO4 and O-Zn termination absorption coefficient using the HSE06 method, which overlaps the standard AM1.5 G solar flux incident.

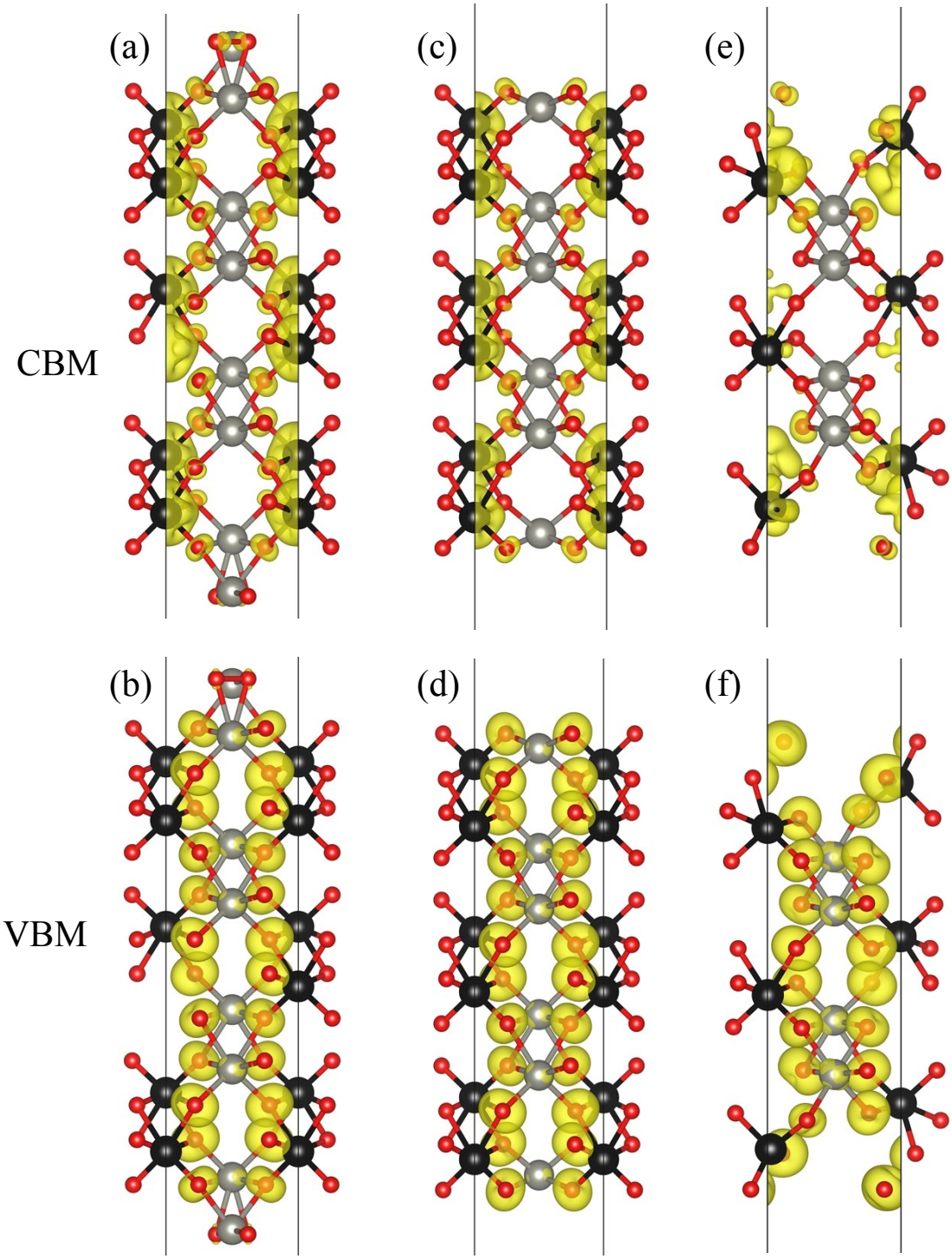


Fig. S5 The side views of partial charge density of the CBM and VBM for the DL-Zn, O-Zn, and DL-W terminations of $ZnWO_4$ (010) surface (a) CBM of DL-Zn, (b) VBM of DL-Zn term., (c) CBM of O-Zn term., (d) VBM of O-Zn term. (e) CBM of DL-Zn term., (f) VBM of DL-Zn term. The isosurface values are 0.0018 e/Å^3. The red, black and gray balls represent O, W, and Zn atoms, respectively.

1. J. Zhang, J. X. Cao, X. Chen, J. W. Ding, P. Zhang and W. Ren, *Phys. Rev. B*, **2015**, 91, 045417.
2. S. Saha, T. P. Sinha and A. Mookerjee, *Phys. Rev. B*, **2000**, 62, 8828-8834.
3. J. Zhang, M. Deng, Y. Yan, T. Xiao, W. Ren and P. Zhang, *Phys. Rev. Appl.*, **2019**, 11, 044052.